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PREPARATION, CHARACTERIZATION AND CRYSTAL STRUCTURES OF ORGANOGERMANIUM DITHIOCARBAMATES AND DITHIOPHOSPHATES

by

© Anil B. Sarkar

A Dissertation

Submitted to the Faculty of Graduate Studies through the Department of Chemistry and Biochemistry in partial fulfilment of the requirements for the Degree of Doctor of Philosophy at the University of Windsor

Windsor, Ontario, Canada

1986

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Windsor, Ontario

April, 1986

Anil B. Sarma

ABSTRACT

Thirty-three germanium derivatives of dithiocarbamic acid and dithiophosphoric acid of the general formula $R_nGeX_{4-n-m}L_m$, where R = CH_3, C_4H_9, X = Cl, Br, I and L = $SC(S)N(CH_3)_2$, $SC(S)N(C_2H_5)_2$, $SP(S)(OCH_3)_2$, $SP(S)(OC_2H_5)_2$, with n = 0 - 4, m = 1 - 3, were synthesized in modest to high yields by reacting salts of the acids with the appropriate germanes. The intermediate dithiocarbamate halides were prepared by exchange reactions with trimethylsilyl bromide and iodide. The products are liquids or crystalline solids and hygroscopic to various degrees. The compounds were characterized by elemental analysis, vibrational and nuclear magnetic resonance spectroscopy, mass spectrometry and by single crystal X-ray structure determinations. For the dithiocarbamates, ir bands for ν(C-N) were observed in the 1570 - 1485 cm^{-1} region, narrowly overlapping the high energy end of the region that indicates monodentate bond formation. However, the ν(C=S) band around 1000 cm^{-1} and ν(Ge-S) around 400 cm^{-1} were in typical regions. The ν(Ge-X) bands showed some unusual features. For the dithiophosphates, the ν(P=S) stretch appeared arround 645 cm^{-1}, while the ν(Ge-S) stretch fluctuated between 400 cm^{-1} and 375 cm^{-1}. The Raman spectra of dithiocarbamates often did not display any clearly defined ν(C-N) stretch, but the ν(C=S) stretches gave intense bands. For the dithiophosphates the ν(P=S) bands were often the strongest. In the ^1H nmr spectra, the chemical shifts of the Ge-CH_3 groups shifted as if the dithiophosphates were equivalent to a chlorine atom, and the

dithiocarbamates were equivalent to a bromine atom. The dithiocarbamate groups, appearing as a singlet or quartets, or the dithiophosphate groups, appearing as a doublet or doublet of quartet due to $^{3}J_{POCH}$ coupling, do not show any significant changes in positions. The $^{13}C\{^{1}H\}$ nmr spectra of dithiocarbamates display δ(C=S) around 195 ppm, not significantly varying from compound to compound. The chemical shifts of Ge-CH_3 groups correspond well with the assumption that the effects of the dithiocarbamate and dithiophosphate groups were equivalent to those of chlorine and bromine atoms respectively. For the dithiophosphates, methoxy (OCH_3) and methyleneoxy (OCH_2) groups often appear as a clear doublet due to $^{2}J_{POC}$ coupling. The results from the ^{31}P nmr spectra were surprising. While most of the compounds show equivalence of dithiophosphate groups, a few of them do not. Nevertheless, the chemical shifts range between 95 and 85 ppm and do not change significantly. The mass spectra of both dithiocarbamates and dithiophosphates showed preferential loss of dithiocarbamate or dithiophosphate groups indicating the ease of dissociation of the Ge-S bond as is to be expected for monodentate attachment. Even in the field ionization mode, the molecular ions were occasionally missing. The crystal structure of chlorodimethyl(*N*,*N*'-dimethyldithiocarbamatogermane), $(CH_3)_2Ge[SC(S)N(CH_3)_2]Cl$, revealed a number of interesting features. The germanium atom is located in the centre of a trigonal bipyramid, with two carbon atoms and one sulfur atom of the dithiocarbamate group in equatorial positions, while the chlorine atom, at an

unusually longer distance, fills the apical site and the second sulfur atom partly occupies the remaining vacant site. The molecule possesses one long and one short Ge–S distance, a short C–N bond and a very long Ge–Cl bond. The short C–N distance, attributed to its partial double bond character, is consistent with the appearance of the ν(C–N) stretch in the infrared spectra around 1500 cm^{-1}. The long Ge–Cl distance accounts for a change in the position of the ν(Ge–Cl) band by 100 cm^{-1} towards the far infrared region. The molecule is assumed to be formed by a nucleophilic attack of the dithiocarbamate group along the C_2 axis bisecting the Cl–Ge–Cl angle in $(CH_3)_2GeCl_2$. One chlorine is pushed away, the other one is bent back to the axial position, making the methyl groups and one sulfur atom lie on the equatorial plane. The second sulfur then moves into the second axial site. A subsequent nucleophilic attack on this molecule would replace the remaining chlorine atom and put the germanium atom in the center of a much distorted octahedron, with four sulfur atoms occupying the equatorial sites and the methyl groups at the vertices. The crystal structure of dimethylbis-(*N*,*N*'-dimethyldithiocarbamatogermane), $(CH_3)_2Ge[SC(S)N(CH_3)_2]_2$, essentially supports this mechanism. The C–Ge–C angle does not open sufficiently to make the methyl groups genuinely trans-octahedral. The structure of dichloromethyl(*N*,*N*'-dimethyl-dithiocarbamato)germane, $CH_3Ge[SC(S)N(CH_3)_2]Cl_2$, was partially solved. Crystals of the compound displayed severe twinning and decay problems, and the structure could not be refined. The

structure, however, is basically similar to that of $(CH_3)_2Ge[SC(S)N(CH_3)_2]Cl$, with one chlorine in the axial and the other in the equatorial position. In sharp contrast to anisobidentate dithiocarbamates, the dithiophosphates are completely monodentate, which is considered a rarity among related compounds. In the crystal structures of triphenyl(*O,O'*-dimethyldithiophosphato)germane, $(C_6H_5)_3Ge[SP(S)(OCH_3)_2]$, diphenylbis(*O,O'*-dimethylthiophosphato)germane, $(C_6H_5)_2Ge[SP(S)(OCH_3)_2]_2$, and phenyltris(*O,O'*-dimethyldithiophosphato)germane, $C_6H_5Ge[SP(S)(OCH_3)_2]_3$, the germanium atom retains its tetrahedral geometry. Not only are the dithiophosphate groups monodentate, but the non-bonding sulfur atoms are turned as far away as possible from the germanium atom.

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CHAPTER I

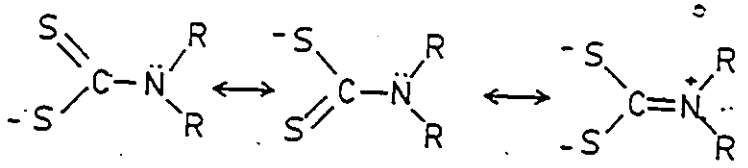
INTRODUCTION

The chemistry of compounds containing dithiocarbamate, $SC(S)NR_2$, or dithiophosphate, $SP(S)(OR)_2$, groups has been an engaging field of research for three-quarters of a century, partly due to the unusual properties of the compounds which pose a challenge to interpretation, and to a greater extent, their relevancy in industry and agriculture. The reaction of an amine with carbon disulfide[1,2] to produce a dithiocarbamate anion and the reaction of an alcohol with phosphorus(V)sulfide[3,4] to give a dithiophosphoric acid are among the earliest reactions ever studied, and yet their metal complexes had not been utilized to their full potential till the late fifties. Zinc, manganese, and iron dithiocarbamates have found extensive use in agriculture and the zinc dithiocarbamates were used as accelerators in rubber vulcanization.[5] Zinc dithiophosphates were tested as petroleum additives and their potential is reflected in hundreds of patents around the world. Both dithiocarbamates and dithiophosphates have been mass produced and attention has also been directed towards structure-function correlations. The structures of $Co[SC(S)N(CH_3)_2]_2NO$ (1962)[6], $Cu_4[SC(S)N(C_2H_5)_2]_4$ (1963)[7] and $K[SP(S)(OCH_3)_2]$ (1962)[8] were presumably among the earliest reports, and ever since a wealth of information has been accumulated. Metal derivatives of dithiocarbamates and dithiophospates have been reviewed in detail.[9-12]

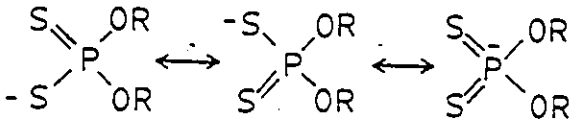
The common strategy for the preparation of dithiophosphate derivatives has been the reactions of metal hydroxides, oxides or chlorides with either the free acids or their salts.[13] However,

for the dithiocarbamates, apart from metathesis, preparative routes involving CS_2 insertion between the metal–nitrogen bond[14] or the photochemical cleavage of tetramethylthiuram disulfide have also been utilized.[15]

The special feature of dithiocarbamate groups is the π-electron flow from the nitrogen atom to the sulfur atoms via a planar π-orbital system.



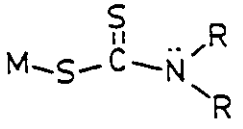
On the other hand, in dithiophosphate groups, π-electrons from the sulfur atoms may be easily accommodated in vacant d-orbitals of the phosphorus atom.

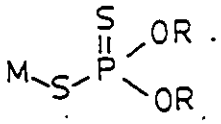


As a result, the dithiocarbamates serve as more effective electron donors than the dithiophosphates. However, the

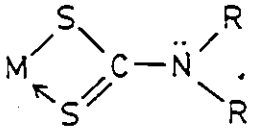
flexibility in electron distribution makes it possible for both groups to stabilize different oxidation states of a number of transition metals.[11] The electron delocalization also determines the bonding mode in a particular compound, monodentate, bidentate, or bridging.

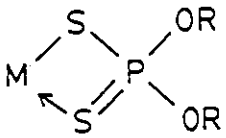
MONODENTATE



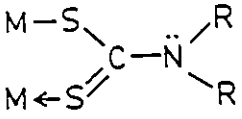


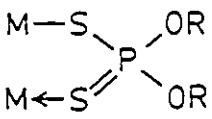
BIDENTATE





BRIDGING





In general, dithiocarbamates and dithiophosphates serve as chelating groups binding through both sulfur atoms as exemplified in $Cr[SC(S)N(C_2H_5)_2]_3$[14] and $Ni[SP(S)(OC_2H_5)_2]_2$.[17] In $Zn_8[SC(S)N(C_2H_5)_2]_8$[18] and $Cu_4[SP(S)(OC_3H_7\text{-}i)_2]_4$,[19] the groups are bridging. In $Cd_2[SP(S)(OC_3H_7\text{-}i)_2]_4$,[20] the dithiophosphate groups are bridging as well as bidentate. Compounds containing monodentate dithiocarbamates and dithiophosphates are relatively rare. Predominantly the mixed ligand complexes prefer to bind through one sulfur only as evidenced in $Pt[SC(S)N(C_2H_5)_2]_2P(C_6H_5)_3$,[21] $W[SC(S)N(CH_3)_2](C_5H_5)(CO)_3$,[15] and in the 2,9-dimethyl-1,10-phenanthroline adduct of $Ni[SP(S)(OCH_3)_2]_2$.[22] In dithiophosphates, structural changes are brought about by variation of the alkoxy group so that $Zn[SP(S)(OC_2H_5)_2]_2$[23] is polymeric, whereas $Zn[SP(S)(OC_3H_7\text{-}i)_2]_2$[20] is dimeric and binuclear. Occasionally the steric requirements of the groups lead to unusual geometry around the metal itself. The structures of $CH_3Sn[SC(S)N(C_2H_5)_2]_3$[24] and $C_6H_9Sn[SC(S)N(C_2H_5)_2]_3$[25] are particularly notable. Both compounds have seven-coordinated pentagonal bipyramidal tin, with the alkyl group occupying an axial site and the sulfur atoms occupying the remaining sites. The structure of $Pb[SP(S)(OC_3H_7\text{-}i)_2]_2$[26] is quite unique with the active lone-pair of lead participating in the creation of pentagonal bipyramidal geometry around lead. It is intriguing that a change in space group occurs with a change in temperature in the structure of $Fe[SC(S)N(C_2H_5)_2]_3$.[27]

It may be obvious from the resonance structures that the

evidence of the bonding mode of the dithiocarbamate groups lies in the ν(C–N) and ν(C=S) stretching frequencies.[28–30] Vibrational data coupled with ^{13}C nmr chemical shifts established the monodentate coordination of one of the dithiocarbamate ligands of $Ru[SC(S)N(CH_3)_2]NO$ in solution.[31] In the same note, it was suggested that the ν(P=S) stretch and the ^{31}P nmr chemical shifts should distinguish between monodentate or bidentate coordination of the dithiophosphate groups.[32] However, in contrast to the extensive vibrational data available, the amount of ^{31}P nmr data of compounds containing dithiophosphate groups is scant.[33]

Among the group 14 (IV) elements, lead and tin derivatives of dithiophosphates[34–42] and dithiocarbamates[43–49] have been extensively studied. By contrast, little is known about germanium analogues[50–52] which might well prove to be of moderate biocidal activity and could possibly be used as oil additives. The objective of this study is to find efficient routes to high yield syntheses of organogermanium derivatives of dithiocarbamic and dithophosphoric acid and fully explore their physical and spectroscopic properties . The compounds are also of interest from the structrual point of view since various modes of bonding are possible. This work presents the synthesis and characterization of eighteen dithiocarbamates and fifteen dithiophosphates of germanium along with six single crystal X–ray structure determinations.

CHAPTER II

EXPERIMENTAL TECHNIQUES AND INSTRUMENTATION

The use of a vacuum line is the standard technique for inorganic reactions especially when the materials are volatile, moisture sensitive, flammable, or of disagreeable odor and unknown toxicity.[53,54] In addition, for small scale reactions, the vacuum method ensures minimal atmospheric contamination and essentially no loss of material. The technique also permits non-destructive spectroscopic characterization of compounds. Accelerated crystallization of compounds, especially for air-sensitive compounds is an additional advantage of the vacuum line technique.

II.1 THE VACUUM LINE

The vacuum line used in this study was constructed from Pyrex glass and consisted of two minor manifolds of a volume of approximately 150 mL each, interconnected by four U traps, and a central manifold leading to a pumping system. (Figure 1) The pumping system was composed of two liquid nitrogen backing traps, a mercury diffusion pump and a rotary oil pump. Pressure readings between 1 - 760 mm Hg (0.13 - 101.33 kPa) were monitored by mercury manometers connected to minor manifolds. A Pirani gauge connected to a central manifold monitored pressures below 1 torr. The normal pressure of the vacuum line was 0.07 torr (9.1×10^{-3} kPa).

II.2 CONSTANT TEMPERATURE COLD BATHS

Cold baths were used to degas material before storage, for separation of volatile components of a mixture by trap to trap distillation, to distil in volatile reactants and solvents or simply to maintain a system at lower temperature. The cold baths used in this study are ice-water (0°C), carbon tetrachloride-liquid nitrogen (-23°C), dry ice-acetone (-78°C), and liquid nitrogen (-196°C).

II.3 THE REACTION VESSEL

All the reactions described in this study were carried out in a special reaction vessel suitable for on-line filtration and subsequent removal of volatile materials. (Figure 2) The reaction vessel was constructed of Pyrex glass and consisted of three parts: part A, where the reaction is carried out, part B, where insoluble materials are separated, and part C, where the volatile materials are evaporated off. The vessel has several beneficial features. Solid starting material can be dried in the same vessel before reaction, and fresh solvent may be reintroduced for recrystallization. In most cases, all the steps starting from the starting material to final product can be done utilizing the same vessel.

II.4 STORAGE VESSELS

The storage vessels were constructed of Pyrex glass. Their shapes and sizes were determined by the nature of the compound

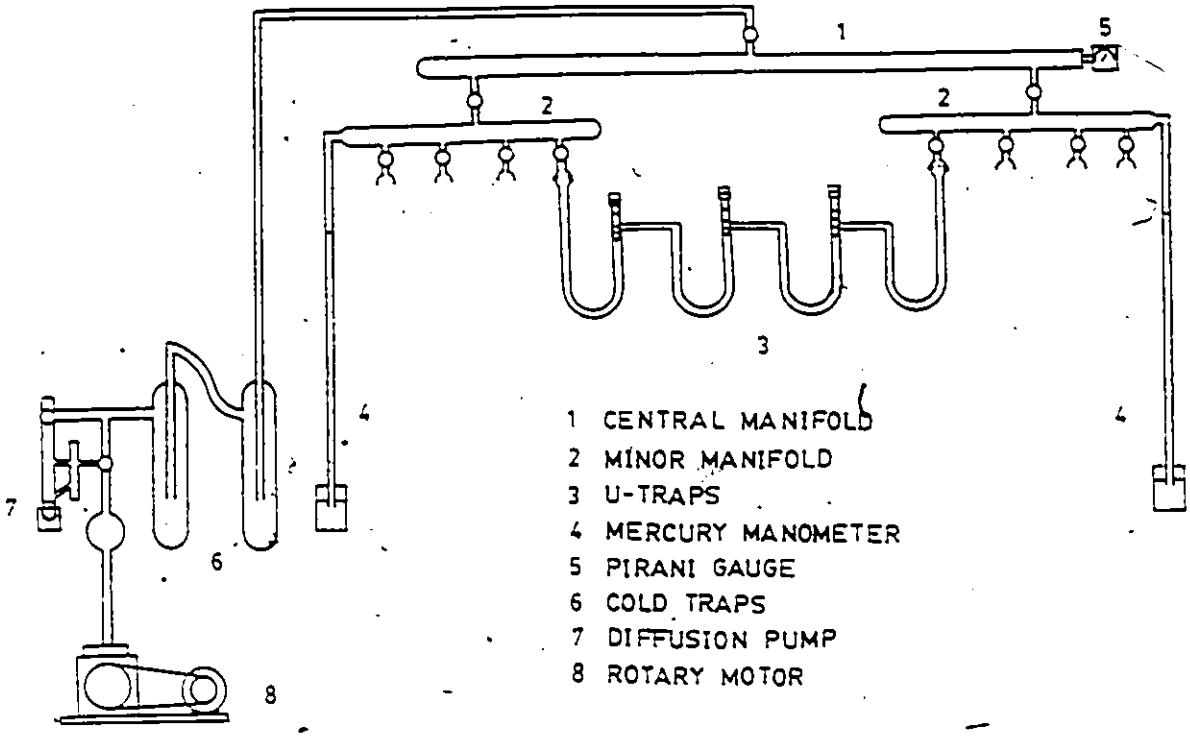


Figure 1 The Vacuum Line.

stored. Volatile compounds, such as $(CH_3)_2GeCl_2$, were stored in type E vessels. Carbon disulfide and $(CH_3)_3GeBr$ were stored in vessels of type D. Low volatile substances were stored in vessels H. Compounds for studying Raman spectra were stored in drawn tubes G. The final products were stored in F, for easy removal of compounds and re-evacuation of the vessel.

II.5 CLEANING OF GLASSWARE

Thorough cleaning of glassware is a key factor for successful synthesis of compounds. Different methods of cleaning were employed. Common cleaning agents were soap-water, acetone, chloroform, dilute hydrofluoric acid (10%). Often aqua regia (3 : 1 mixture of hydrochloric and nitric acid) and ethanol-nitric acid solution were needed. The latter mixture often resulted in violent reactions and so were carried out in the fume hood. After cleaning, the glassware was rinsed with water and acetone, and dried in the oven at 100°C.

II.6 INSTRUMENTATION AND PHYSICAL METHODS

A: Nuclear Magnetic Resonance Spectroscopy

^1H nmr spectra of the compounds were recorded on a Varian EM 360 (60 MHz) spectrometer in CS_2 or $CDCl_3$ solutions using tetramethylsilane (TMS, 0.0 ppm) as internal standard. For salts, deuterium oxide was used as solvent and sodium trimethylsilylpropanoate (TSP, 0.0 ppm) served as an internal standard. $^{13}C\{^1H\}$ nmr spectra (22.64 MHz) and ^{31}P (36.44 MHz) nmr spectra

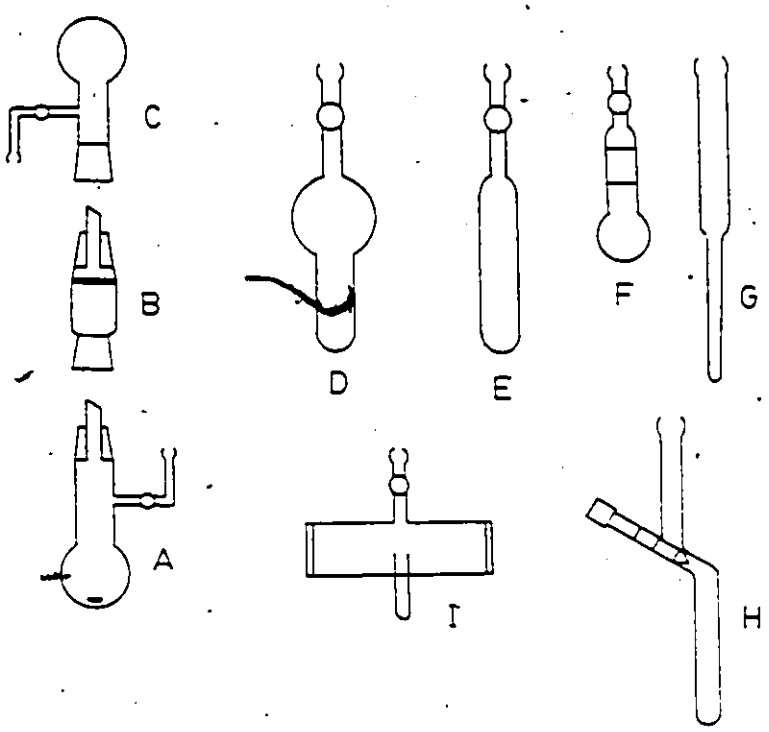


Figure 2 Reaction and Storage Vessels.

were recorded on a Bruker CXP 100 FT spectrometer in $CDCl_3$ solutions. For ^{13}C nmr spectra the central line of the $CDCl_3$ resonance at 77.12 ppm (1746 Hz) was used as internal standard. Salts were run in deuterium oxide with dioxane (67.4 ppm, 1529.5 Hz) as internal standard. The ^{31}P nmr spectra were recorded in $CDCl_3$ or in CS_2 with 85% phosphoric acid as external standard (0.0 ppm).

B. Vibrational Spectroscopy

The infrared spectra were recorded on a Perkin-Elmer 180 double-beam spectrophotometer or on a Nicolet 5DX FT spectrometer as CsI pellets, nujol mulls and CS_2 or CCl_4 solutions on CsI plates. Gas phase infrared spectra were recorded using a 10 cm cell, fitted with CsI windows and a condensing finger, at normal vacuum line pressure. The samples for Raman spectra were sealed in capillaries and the spectra were measured on a Spectra-Physics 700 using the 4880 Å exciting line or on a Spectra-Physics 164 using the 5145 Å exciting line of an argon ion laser.

C. Mass Spectrometry

The mass spectra were recorded on a Varian GMAT CH5 double-focusing spectrometer equipped with an INCOS 2000 computer system using the electron impact (EI) mode operating at 70 eV. A number of compounds were recorded also in the field ionization (FI) mode due to a lack of their volatility.

D. X-Ray Crystallography

Suitable crystals were sealed in capillary tubes and mounted on a Syntex $P2_1$ diffractometer equipped with a

scintillation counter and a graphite monochromator. The unit cell dimensions were determined from the rotation and axial photographs and refined from a few high angle reflections. The data were collected using the $\theta - 2\theta$ scan technique. The structures were determined by sharpened Patterson synthesis using *SHELX* and refined by full- matrix least-squares methods.

E. Melting Points

The melting points were determined on a Fisher-Johns melting point apparatus. The samples were placed between microscope cover glass and the points at which the compounds completely liquified were recorded.

F. Refractive Indices

The refractive indices of liquid samples were measured on a Bausch and Lomb refractometer and corrected to 25°C ($\pm 4 \times 10^{-4}$ per °C).

G. Elemental Analyses

The elemental analyses of the compounds were performed either by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada or by Galbraith Laboratories Inc., Knoxville, Tennessee, USA.

H. Density Measurements

Densities for a number of crystals were needed for X-ray structure determinations and were measured by the floation method.

CHAPTER III

CHEMICALS AND SOLVENTS

In view of the moisture sensitivity of the germanium compounds, all the starting materials were manipulated with utmost care. The compounds listed in this section were commercially available or had well established preparative routes. The purity of the compounds were checked by infrared, Raman and nuclear magnetic resonance spectroscopy. Solid compounds were also checked by melting point determinations.

Acetone, CH_3COCH_3: Fisher Scientific; anhydrous quality stored over drierite.

Ammonium *O,O'*-diethyldithiophosphate, $NH_4SP(S)(OC_2H_5)_2$: Aldrich Chemical; dried prior to use; checked by ir, ^{13}C nmr and ^{31}P nmr.

Ammonium *O,O'*-dimethyldithiophosphate, $NH_4SP(S)(OCH_3)_2$: Aldrich Chemical; dried prior to use; checked by ir, ^{13}C nmr and ^{31}P nmr.

Benzene, C_6H_6: Fisher Scientific; distilled prior to use and dried with metallic sodium, degassed at -78°C and stored in vessel A over molecular sieves.

Bromotrimethylgermane, $(CH_3)_3GeBr$: Alfa Inorganics; degassed at -78°C and stored in vessel D at ambient temperature; checked by ir, Raman and ^1H nmr.

Bromotrimethylsilane, $(CH_3)_3SiBr$: Petrarch Systems; degassed at -78°C and stored at ambient temperature in vessel E; checked by ir and ^1H nmr.

Bromotriphenylgermane, $(C_6H_5)_3GeBr$: Alfa Inorganics; used as supplied; checked by ir and ^1H nmr.

Carbon disulfide, CS_2: Fisher Scientific; dried over P_2O_5 and distilled, degassed at −196°C and stored in vessel D; checked by ir.

Carbon tetrachloride, CCl_4: Fisher Scientific; dried over P_2O_5 and distilled, degassed at −196°C and stored in vessel E; checked by ir.

Chloroform, $CHCl_3$; Fisher Scientific; dried with calcium chloride and distilled.

Dichlorodimethylgermane, $(CH_3)_2GeCl_2$: Alfa Inorganics; degassed at −78°C and stored in vessel E; checked by ir and ^1H nmr.

Dichlorodiphenylgermane, $(C_6H_5)_2GeCl_2$: Alfa Inorganics; used as supplied; stored in vessel H; checked by ir, Raman and ^1H nmr.

Diethylamine, $(C_2H_5)_2NH$: Fisher Scientific; used as obtained; checked by ^1H nmr.

N,N'-Diethylammonium *N,N*-diethyldithiocarbamate, $(C_2H_5)_2NH_2$-$[SC(S)N(C_2H_5)_2]$: Prepared by the reaction of $(C_2H_5)_2NH$ with excess CS_2 at 0°C; checked by ir, ^1H nmr and mass spectrometry.

N,N'-Diethyldithiocarbamic acid *S*-ethyl ester, $(C_2H_5)_2NC(S)S$-(C_2H_5): Prepared by reacting $(C_2H_5)_2NCS(S)Na$ and C_2H_5Br (2 mmol each) in diethyl ether at ambient temperature; checked by ir, ^1H nmr and mass spectrometry.

Diethyl ether, $(C_2H_5)_2O$: Fisher Scientific; anhydrous quality used as obtained.

Dimethylamine hydrochloride, $(CH_3)_2NH_2Cl$: Fisher Scientific; used as obtained; checked by ^1H nmr.

N,N'-Dimethylammonium *N,N'*-dimethyldithiocarbamate, $(CH_3)_2NH_2$-$[SC(S)N(CH_3)_2]$: Prepared by reaction of $(CH_3)_2NH$ (10 mmol) with CS_2 (5 mmol) in chloroform at 0°C; checked by ir, ^1H nmr and mass spectrometry.

N,N'-Dimethyldithiocarbamic acid S-methyl ester, $(CH_3)_2NC(S)SCH_3$: Prepared by reacting equimolar amounts of $(CH_3)_2NCS(S)Na$ and CH_3I in CS_2 at 0°C; checked by ir, ^1H nmr and mass spectrometry.

Diphenylbis(*O,O'*-diethyldithiophosphato)tin, $(C_6H_5)_2Sn[SP(S)-(OC_2H_5)_2]$: Prepared by reaction of $(C_6H_5)_2SnCl_2$ (1.5 mmol) with excess $NH_4[SP(S)(OC_2H_5)_2]$ (3.5 mmol) in benzene; checked by ^1H nmr, ^{13}C nmr and ^{31}P nmr.

Ethylbromide, C_2H_5Br: Fisher Scientific; used as obtained; checked by ^1H nmr.

n-Hexane, C_6H_{14}: Fisher Scientific; dried over metallic sodium.

Iodomethane, CH_3I: Fisher Scientific; degassed at -196°C and stored in vessel E.

Iodotrimethylsilane, $(CH_3)_3SiI$: Petrarch Systems; degassed at -196°C and stored in vessel E in the refrigerator; checked by ^1H nmr.

Ligroin (37 - 54°C): Fisher Scientific; distilled and stored over metallic sodium.

Methylene chloride, CH_2Cl_2: Fisher Scientific; dried over P_2O_5 and distilled.

Sodium *N,N'*-diethyldithiocarbamate, $(C_2H_5)_2NCS(S)Na$: Aldrich Chemical; stored in a desiccator, dried prior to use on a vacuum line; checked by ir, ^1H nmr and ^{13}C nmr.

Sodium *N,N'*-dimethyldithiocarbamate, $(CH_3)_2NCS(S)Na$: Kodak; stored in a desiccator, dried water free on a vacuum line prior to use; checked by ir, Raman, ^1H nmr and ^{13}C nmr.

Tetrabromogermane, $GeBr_4$: Alfa Inorganics; used as obtained.

Tetrachlorogermane, $GeCl_4$: Alfa Inorganics; degassed at -78°C and stored in vessel E; checked by ir.

Tetraiodogermane, GeI_4: Alfa Inorganics; used as obtained.

Trichloromethylgermane, CH_3GeCl_3: Alfa Inorganics; purified by trapping at -23°C, degassed at -78°C and stored in vessel E in the refrigerator; checked by ir and ^1H nmr.

Trichlorophenylgermane, $C_6H_5GeCl_3$: Strem Chemicals; used as obtained; stored in vessel H; checked by ir, Raman and ^1H nmr.

Triphenyl (*O,O'*-dimethyldithiophosphato)tin, $(C_6H_5)_3Sn[SP(S)-(OCH_3)_2]$: Prepared by reaction of equimolar amounts of $(C_6H_5)_3SnCl$ with $NH_4[SP(S)(OCH_3)_2]$ (2 mmol each) in benzene; checked by ^1H nmr, ^{13}C nmr and ^{31}P nmr.

In determining the purity of compounds, ^1H nmr spectroscopy was the most useful means, since proton containing impurities as low as 1% could be easily detected.

CHAPTER IV

THE PREPARATION OF ORGANOGERMANIUM DERIVATIVES OF DITHIOCARBAMATES

The lack of stability of the dithiocarbamic acids has deprived the chemist of a generally useful route to the synthesis of metal complexes that involves the free acid. In fact, the preparations of dithiocarbamate compounds have been predominantly via alkali metal salts[55] or an *in situ* reaction of a metal salt with a dialkylamine and carbon disulfide[28] as exemplified below:

$$TiCl_4 + 4NaS\overset{S}{=}CNMe_2 \xrightarrow{\text{BENZENE}} Ti[S\overset{S}{=}CNMe_2]_4 + 4NaCl\downarrow$$

$$R_3SnOH + CS_2 + HNR'_2 \longrightarrow R_3Sn[S\overset{S}{=}CNR'_2] + H_2O$$

The absence of a general route has led to novel synthetic techniques. For example copper, silver, gold[54] and molybdenum[57] complexes have been prepared by oxidative addition of tetraalkyl-thiuram disulfide.

$$4Cu + 2[S\overset{S}{=}CNR_2]_2 \xrightarrow{CHCl_3} Cu_4[S\overset{S}{=}CNR_2]_4$$

$$2Mo(CO)_6 + 3[S\overset{S}{=}CNR_2]_2 \xrightarrow{\text{TOLUENE}} Mo_2[S\overset{S}{=}CNR_2]_6 + 12CO$$

Particularly interesting is the synthesis of phosphorus dithiocarbamates,[58] a non-metallic system, where carbon disulfide is inserted in two steps between the P-N bond of hexamethylphosphorus triamide (HMPT). A large number of compounds have been synthesized involving amino-metallation of carbon disulfide.[59,60]

$$R_3SiNR'_2 + CS_2 \longrightarrow R_3Si[S\overset{S}{\overset{\|}{C}}NR'_2]$$

$$As[NMe_2]_3 + 3CS_2 \longrightarrow As[S\overset{S}{\overset{\|}{C}}NMe_2]_3$$

The mechanism of amino-metallation involves an electrophilic attack of CS_2 on nitrogen resulting in the formation of a cyclic intermediate.[63]

$$Me_3Sn\text{–}\overset{\curvearrowright}{N}Me_2 \longrightarrow \left[Me_3Sn\cdots NMe_2\right] \longrightarrow Me_3SnS\overset{S}{\overset{\|}{C}}NMe_2$$
$$\underset{S=C=S}{\overset{\curvearrowleft}{}}$$

The quantitative precipitation of chromium(III)dithiocarbamates by addition of the ligand to chromium(III) ions has been suggested as a method for the determination of chromium.[61] The following is an interesting example of the transfer of an entire dithiocarbamate group from an organometallic moiety.[62]

$$(C_5H_5)W(CO)_3Cl + Me_3Sn[S\overset{S}{\overset{\|}{C}}NMe_2] \longrightarrow (C_5H_5)W(CO)_2[S\overset{S}{\overset{\|}{C}}NMe_2] + CO + Me_3SnCl$$

Notable is the absence of electrochemical methods. Only $[R_2NC(S)S]_2$ species, which are non-metallic dithiocarbamates, have been prepared by electrochemical oxidative coupling of

dithiocarbamate salts.[43]

The primary synthetic strategy adopted for the formation of the Ge-S linkage in this study was by direct reaction of the sodium salt of dithiocarbamic acid with germanes. For bromo and iodo intermediates, exchange reactions with trimethylsilyl bromide and iodide were utilized. For the preparation of *N,N'*-dimethyl- dithiocarbamate derivatives, the reactions depicted in Scheme 1 were followed.

SCHEME 1

a. $Me_3GeBr + Na[S_2CNMe_2] \longrightarrow \underset{1}{Me_3Ge[S_2CNMe_2]} + NaBr$

b. $Me_2GeCl_2 + Na[S_2CNMe_2] \longrightarrow \underset{2}{Me_2Ge[S_2CNMe_2]Cl} + NaCl$

$Me_2Ge[S_2CNMe_2]Cl + Me_3SiBr \longrightarrow \underset{2a}{Me_2Ge[S_2CNMe_2]Br} + Me_3SiCl$

$Me_2Ge[S_2CNMe_2]Cl + Me_3SiI \longrightarrow \underset{2a}{Me_2Ge[S_2CNMe_2]I} + Me_3SiCl$

$Me_2Ge[S_2CNMe_2]Br + Me_3SiI \longrightarrow \underset{2b}{Me_2Ge[S_2CNMe_2]I} + Me_3SiBr$

c. $Me_2GeCl_2 + 2\ Na[S_2CNMe_2] \longrightarrow \underset{3}{Me_2Ge[S_2CNMe_2]_2} + 2\ NaCl$

d. $MeGeCl_3 + Na[S_2CNMe_2] \longrightarrow \underset{4}{MeGe[S_2CNMe_2]Cl_2} + NaCl$

$MeGe[S_2CNMe_2]Cl_2 + 2\ Me_3SiBr \longrightarrow \underset{4a}{MeGe[S_2CNMe_2]Br_2} + 2\ Me_3SiCl$

e. $Ph_3GeCl + Na[S_2CNMe_2] \longrightarrow \underset{5}{Ph_3Ge[S_2CNMe_2]} + NaCl$

f. $Ph_2GeCl_2 + Na[S_2CNMe_2] \longrightarrow \underset{6}{Ph_2Ge[S_2CNMe_2]Cl} + NaCl$

Preparation of trimethyl(*N*,*N*'-dimethyldithiocarbamato)germane (1), $(CH_3)_3Ge[SC(S)N(CH_3)_2]$.

The salt, $(CH_3)_2NSC(S)Na$ (0.514 g, 3.60 mmol) was dried for several hours before $(CH_3)_3GeBr$ (4.0 mmol) was distilled onto it. Subsequently, CS_2 (3 mL) was distilled into the reaction vessel. The mixture was allowed to gradually warm up and was maintained at 0°C with moderate stirring. After 4 h, solid NaBr was filtered off and the filtrate was very slowly evaporated on the vacuum line. Needle shaped white crystals were formed in the reaction vessel. Yield 56%, mp 30°C. Anal. Calcd for $C_6H_{15}NS_2Ge$: C, 30.29; H, 6.36; N, 5.89. Found: C, 30.18; H, 6.37; N, 6.19.

Preparation of chlorodimethyl(*N*,*N*'-dimethyldithiocarbamato)-germane (2), $(CH_3)_2Ge[SC(S)N(CH_3)_2]Cl$.

The germane, $(CH_3)_2GeCl_2$ (2.74 mmol) along with the solvent, CS_2 (4mL) was distilled onto dry $(CH_3)_2NSC(S)Na$ (0.392 g, 2.74 mmol). The reaction mixture was warmed until the reactants had mixed well, stirred, and then maintained at −23°C. After 2 h, solid NaCl was filtered off and the filterate was allowed to evaporate gradually. The white crystals thus obtained were washed with cold *n*-hexane and dried. Yield 50%, mp 56°C. Anal. Calcd for $C_5H_{12}NS_2GeCl$: C, 23.25; H, 4.68; N, 5.42. Found: C, 23.11; H, 4.82; N, 5.84.

Preparation of bromodimethyl(*N*,*N*'-dimethyldithiocarbamato)germane (2a), $(CH_3)Ge[SC(S)N(CH_3)_2]Br$.

Excess $(CH_3)_3SiBr$ (2.0 mmol) and CS_2 (3 mL) were added to $(CH_3)_2Ge[SC(S)N(CH_3)_2]Cl$ (0.254 g, 0.98 mmol) by distillation into a trap at liquid nitrogen temperature. The solution was warmed to 0°C and maintained at this temperature for 12 h with occasional stirring. Finally, the mixture was allowed to evaporate and the product was dissolved in *n*-hexane and recrystallized in a refrigerator to obtain diamond shaped crystals of pure $(CH_3)_2Ge[SC(S)N(CH_3)_2]Br$. Yield 33%, mp 84°C. Anal. Calcd for $C_5H_{12}NS_2GeBr$: C, 19.83; H, 4.00; N, 4.63. Found: C, 19.75; H, 3.97; N, 4.67.

Preparation of iododimethyl(*N*,*N*'-dimethyldithiocarbamato)germane (2b), $(CH_3)_2Ge[SC(S)N(CH_3)_2]I$.

Excess $(CH_3)_3SiI$ (1.9 mmol) and CS_2 (3.5 mL) were distilled onto freshly prepared $(CH_3)_2Ge[SC(S)N(CH_3)_2]Cl$ (0.260 g, 1.01 mmol). The vessel was warmed up and the contents were stirred for 12 h at 0°C. On evaporation, a slightly colored product was obtained, which was dissolved in an *n*-hexane and ether mixture and was allowed to recrystallize in the refrigerator. Yield 38%, mp 97°C. Anal. Calcd for $C_5H_{12}NS_2GeI$: C, 17.17; H, 3.46; N, 4.01. Found: C, 17.38; H, 3.52; N, 3.92.

Alternatively, $(CH_3)_3SiI$ (1 mmol) and CS_2 (1mL) were condensed onto freshly prepared $(CH_3)_2Ge[SC(S)N(CH_3)_2]Br$ (0.151 g, 0.50 mmol) and stirred for 5 h. On slow evaporation, crystals

of $(CH_3)_2Ge[SC(S)N(CH_3)_2]I$ appeared, which were washed with *n*-hexane and dried. Yield 45%.

Preparation of dimethylbis(*N*,*N*'-dimethyldithiocarbamato)germane (3), $(CH_3)_2Ge[SC(S)N(CH_3)_2]_2$.

The germane $(CH_3)_2GeCl_2$ (1.5 mmol) and CS_2 (3 mL) were distilled in sequence onto previously dried $(CH_3)_2NCS(S)Na$ (0.520 g, 3.63 mmol). The reaction vessel was warmed to 0°C and the contents stirred vigorously for 12 h. The reaction mixture was occasionally cooled (to ca. −10°C) to slow down the reaction. Finally, the solid NaCl was removed by filtration and the filtrate was allowed to evaporate. The fleecy crystals of the product thus obtained were recrystallized from CS_2 in the refrigerator to give long white needles. Yield 51%, mp 174°C. Anal. Calcd for $C_8H_{16}N_2S_4Ge$: C, 28.01; H, 5.29; N, 8.16. Found: C, 28.14; H, 5.38; N, 8.07.

Preparation of dichloromethyl(*N*,*N*'-dimethyldithiocarbamato)-germane (4), $CH_3Ge[SC(S)N(CH_3)_2]Cl_2$.

The germane, CH_3GeCl_3 (2 mmol) and the solvent, CS_2 (3 mL) were distilled onto previously dried $(CH_3)_2NCS(S)Na$ (0.529 g, 3.69 mmol). The reaction vessel was maintained in liquid nitrogen fumes (ca. −20°C) for 15 minutes. As soon as the color of the mixture started to change, it was filtered and the solvent was evaporated slowly while the vessel was kept cool (ca. −10°C). The transparent yellowish colored crystals thus obtained were

immediately pumped on the vacuum line to dry. Yield 35%, mp 52°C. Anal. Calcd for $C_4H_9NS_2GeCl_2$: C, 17.23; H, 3.26; N, 5.20. Found: C, 17.37; H, 3.61; N, 5.14.

Preparation of dibromomethyl(*N*,*N*'-dimethyldithiocarbamato)germane (4a), $CH_3Ge[SC(S)N(CH_3)_2]Br_2$.

To the dry salt, $(CH_3)_2NCS(S)Na$ (0.558 g, 3.90 mmol) the germane, CH_3GeCl_3 (3 mmol) and CS_2 (2 mL) were added in sequence. The reaction vessel was allowed to warm to −20°C and the mixture was moderately stirred. After 15 minutes the mixture was filtered and the solvent was pumped off as rapidly as possibly prior to $(CH_3)_3SiBr$ (2 mmol) and CS_2 (1 mL) being distilled onto the crystalline residue. The solution was left for 24 h in liquid nitrogen fumes (ca. −20°C). The solvent and the excess $(CH_3)_3SiBr$ were then pumped off very slowly, while keeping the vessel cool (ca. −10°C), and white fleecy crystals of $CH_3Ge[SC(S)N(CH_3)_2]Br_2$ were obtained. Yield 30%, mp 60°C. Anal. Calcd for $C_4H_9NS_2GeBr_2$: C, 13.07; H, 2.47; N, 3.81. Found: C, 13.11; H, 2.55; N, 3.87.

Attempts to prepare $CH_3Ge[SC(S)N(CH_3)_2]I_2$ by a similar exchange reaction with $(CH_3)_3SiI$ resulted in a mixture of products that could not be clearly identified.

Attempted preparation of chloromethylbis(*N*,*N*'-dimethyldithiocarbamato)germane, $CH_3Ge[SC(S)N(CH_3)_2]_2Cl$, and methyltris(*N*,*N*'-dimethyldithiocarbamato)germane, $CH_3Ge[SC(S)N(CH_3)_2]_3$.

An excess of $(CH_3)_2NCS(S)Na$ was treated with CH_3GeCl_3 in an attempt to prepare the bis and tris derivatives. However, the only product that could be identified was $CH_3Ge[SC(S)N(CH_3)_2]Cl_2$.

Attempted preparation of tetrakis(*N*,*N*'-dimethyldithiocarbamato)germane, $Ge[SC(S)N(CH_3)_2]_4$, and the intermediate compounds, $Ge[SC(S)N(CH_3)_2]_xCl_{4-x}$.

No reaction occurred between $GeCl_4$ and $(CH_3)_2NSC(S)Na$ under conditions similar to those previously described for the formation of $(CH_3)_2Ge[SC(S)N(CH_3)_2]_2$.

Preparation of triphenyl(*N*,*N*'-dimethyldithiocarbamato)germane (5), $(C_6H_5)_3Ge[SC(S)N(CH_3)_2]$.

Dry $(CH_3)_2NSC(S)Na$ (0.205 g, 1.43 mmol) and $(C_6H_5)_3GeCl$ (0.349 g, 1.03 mmol) were mixed together in the evacuated reaction vessel and the solvent, CS_2 (3.5 mL) was distilled onto the mixture. The reaction vessel was allowed to warm up to ambient temperature and stirred for 4 h. The solid NaCl and the unreacted salt, $(CH_3)_3NSC(S)Na$ were separated by filtration and the filtrate was allowed to evaporate under vacuum. A foamy viscous product thus obtained was dissolved in fresh CS_2 and on slow evaporation of the solvent white crystals appeared. The crystals were washed with *n*-hexane and dried. Yield 60%,

mp 160°C. Anal. Calcd for $C_{21}H_{21}NS_2Ge$: C, 59.47; H, 4.99; N, 3.30. Found: C, 59.25; H, 5.37; N, 3.24.

Preparation of chlorodiphenyl(*N*,*N*'-dimethyldithiocarbamato)-germane (6), $(C_6H_5)_2Ge[SC(S)N(CH_3)_2]Cl$.

To the dry salt, $(CH_3)_2NSC(S)Na$ (0.574 g, 4.01 mmol) a cold solution of $(C_6H_5)_2GeCl_2$ (0.533 g, 1.79 mmol) and CS_2 (5 mL) was added under a nitrogen atmosphere. The mixture was immediately frozen and the reaction vessel was evacuated. The contents were gradually warmed up to ambient temperature and were stirred vigorously for 3 h. The reaction mixture was filtered and the filtrate was evaporated under vacuum to give a solid which was dissolved in chloroform and recrystallized. Yield 22%, mp 112°C. Anal. Calcd for $C_{15}H_{14}NS_2GeCl$: C, 47.10; H, 4.22; N, 3.66. Found: C, 47.60; H, 4.47; N, 3.62.

Attempts to prepare $(C_6H_5)_2Ge[SC(S)N(CH_3)_2]_2$ by a similar method using an excess of the salt only resulted in the formation of the monosubstituted compound, $(C_6H_5)_2Ge[SC(S)N(CH_3)_2]Cl$.

Attempted preparation of phenyltris(*N*,*N*'-dimethyldithiocarbamato)germane, $C_6H_5Ge[SC(S)N(CH_3)_2]_3$, and the intermediates, $C_6H_5Ge[SC(S)N(CH_3)_2]_xCl_{3-x}$.

An excess of the salt, $(CH_3)_2NSC(S)Na$ was treated with $C_6H_5GeCl_3$ in CS_2. Viscous mixtures were obtained, which could not be clearly identified.

For the synthesis of analogous *N,N'*-diethyldithiocarbamato derivatives, essentially similar procedures were followed (Scheme 2). The salt, $(C_2H_5)_2NSC(S)Na$, often needed to be crushed for thorough drying and mixing during the reactions.

SCHEME 2

a. $Me_3GeBr + Na[S_2CNEt_2] \longrightarrow \underset{7}{Me_3Ge[S_2CNEt_2]} + NaBr$

b. $Me_2GeCl_2 + Na[S_2CNEt_2] \longrightarrow \underset{8}{Me_2Ge[S_2CNEt_2]Cl} + NaCl$

$\underset{8}{Me_2Ge[S_2CNEt_2]Cl} + Me_3SiBr \longrightarrow \underset{8a}{Me_2Ge[S_2CNEt_2]Br} + Me_3SiCl$

$\underset{8}{Me_2Ge[S_2CNEt_2]Cl} + Me_3SiI \longrightarrow \underset{8b}{Me_2Ge[S_2CNEt_2]I} + Me_3SiCl$

$\underset{8a}{Me_2Ge[S_2CNEt_2]Br} + Me_3SiI \longrightarrow \underset{8b}{Me_2Ge[S_2CNEt_2]I} + Me_3SiBr$

c. $MeGeCl_3 + Na[S_2CNEt_2] \longrightarrow \underset{9}{MeGe[S_2CNEt_2]Cl_2} + NaCl$

$\underset{9}{MeGe[S_2CNEt_2]Cl_2} + 2\,Me_3SiBr \longrightarrow \underset{9a}{MeGe[S_2CNEt_2]Br_2} + 2\,Me_3SiCl$

d. $MeGeCl_3 + 3\,Na[S_2CNEt_2] \longrightarrow \underset{10}{MeGe[S_2CNEt_2]_3} + 3\,NaCl$

e. $Ph_3GeCl + Na[S_2CNEt_2] \longrightarrow \underset{11}{Ph_3Ge[S_2CNEt_2]} + NaCl$

f. $Ph_2GeCl_2 + 2\,Na[S_2CNEt_2] \longrightarrow \underset{12}{Ph_2Ge[S_2CNEt_2]_2} + 2\,NaCl$

Preparation of trimethyl(*N*,*N*'-diethyldithiocarbamato)germane (7), $(CH_3)_3Ge[SC(S)N(C_2H_5)_2]$.

To the previously dried salt, $(C_2H_5)_2NSC(S)Na$ (0.457 g, 2.67 mmol), $(CH_3)_3GeBr$ (2 mmol) and CS_2 (2.5 mL) were distilled on in sequence. The vessel was warmed up to melt the solvent and the mixture was stirred moderately for 5 h, while keeping the vessel cool (ca. −10°C). The mixture was filtered and the solution was allowed to evaporate under vacuum to obtain pure $(CH_3)_3Ge[SC(S)N(C_2H_5)_2]$, as a clear liquid. Yield 63%, η 1.5628. Anal. Calcd for $C_8H_{17}NS_2Ge$: C, 36.13; H, 7.20; N, 5.27. Found: C, 35.80; H, 7.05; N, 5.22.

Preparation of chlorodimethyl(*N*,*N*'-diethyldithiocarbamato)germane (8), $(CH_3)_2Ge[SC(S)N(C_2H_5)_2]Cl$.

The germane, $(CH_3)_2GeCl_2$ (1.5 mmol) and CS_2 (3 mL) were condensed onto dry $(C_2H_5)_2NCS(S)Na$ (0.530 g, 3.09 mmol) at −196°C. The mixture was allowed to gradually warm up to ambient temperature and was stirred for 4 h with occasional cooling to ca. −20°C. NaCl and the unreacted carbamate salt were separated by filtration and the filtrate was evaporated under vacuum. The solid residue thus obtained was dissolved in fresh CS_2 and recrystallized by slowly pumping off the solvent on the vacuum line. Yield 66%, mp 51°C. Anal. Calcd for $C_7H_{14}NS_2GeCl$: C, 29.36; H, 5.63; N, 4.89. Found: C, 29.39; H, 5.71; N, 4.77.

Preparation of bromodimethyl(*N*,*N*'-diethyldithiocarbamato)germane (8a), $(CH_3)_2Ge[SC(S)N(C_2H_5)_2]_2Br$.

Excess $(CH_3)_3SiBr$ (2 mmol) and CS_2 (1 mL) were distilled onto freshly prepared $(CH_3)_2Ge[SC(S)N(C_2H_5)_2]Cl$ (0.271 g, 0.95 mmol). The solution was held at 0°C and stirred for 3 h. The volatile reagents and solvent were slowly pumped off and crystals of pure $(CH_3)_2Ge[SC(S)N(C_2H_5)_2]Br$ appeared. The product was washed with *n*-hexane and dried. Yield 47%, mp 86°C. Anal. Calcd for $C_7H_{14}NS_2GeBr$: C, 25.41; H, 4.88; N, 4.24. Found: C, 25.14; H, 4.69; N, 4.17.

Preparation of iododimethyl(*N*,*N*'-diethyldithiocarbamato)germane (8b), $(CH_3)_2Ge[SC(S)N(C_2H_5)_2]I$.

Freshly prepared $(CH_3)_2Ge[SC(S)N(C_2H_5)_2]Cl$ (0.215 g, 0.75 mmol) was dissolved in $(CH_3)_3SiI$ (1.2 mmol) and CS_2 (1 mL), and was allowed to react for 3 h with moderate stirring at 0°C. The volatile materials were slowly pumped off to obtain yellowish transparent crystals. The crystals were washed with cold *n*-hexane and dried under vacuum. Yield 55%, mp 96°C. Anal. Calcd for $C_7H_{14}NS_2GeI$: C, 22.25; H, 4.27; N, 3.71. Found: C, 22.29; H, 4.14; N, 3.68.

Alternatively, excess $(CH_3)_3SiI$ (1 mmol) and CS_2 (1 mL) were distilled onto freshly prepared $(CH_3)_2Ge[SC(S)N(C_2H_5)_2]Br$ (0.116 g, 0.50 mmol). The solution was stirred for 2 h at 0°C and the volatile compounds were pumped off. The solid product was dissolved in fresh CS_2 and the solvent gradually evaporated

under vacuum to obtain pure crystals of $(CH_3)_2Ge[SC(S)N(C_2H_5)_2]I$. Yield 50%.

Attempted preparation of dimethylbis(*N*,*N*'-diethyldithiocarbamato)germane, $(CH_3)_2Ge[SC(S)N(C_2H_5)_2]_2$.

Excess salt, $(C_2H_5)_2NCS(S)Na$ was treated with $(CH_3)_2GeCl_2$ in CS_2. Only the monosubstituted product, $(CH_3)_2Ge[SC(S)NC_2H_5)_2]Cl$ was obtained. Prolonged reaction times lead to the formation of mixtures which could not be identified.

Preparation of dichloromethyl(*N*,*N*'-diethyldithiocarbamato)germane (9), $CH_3Ge[SC(S)N(C_2H_5)_2]Cl_2$.

To the dry crushed salt, $(C_2H_5)_2NCS(S)Na$ (0.541 g, 3.15 mmol), the germane, CH_3GeCl_3 (2 mmol) and CS_2 (5 mL) were added in sequence at -196°C. The reaction vessel was maintained in liquid nitrogen fumes (ca. -20°C) for 15 minutes to melt CS_2 and CH_3GeCl_3. The mixture was stirred, and as soon as the color of the mixture started to turn yellowish it was immediately filtered. The solvent was slowly evaporated under vacuum while keeping the vessel cool (ca. -10°C) and slightly yellow colored crystals appeared. Yield 40%, mp 42°C. Anal. Calcd for $C_6H_{13}NS_2GeCl_2$: C, 23.49; H, 4.27; N, 4.57. Found: C, 23.26; H, 4.34; N, 4.39.

Preparation of dibromomethyl(*N*,*N*'-diethyldithiocarbamato)germane (9a), $CH_3Ge[SC(S)N(C_2H_5)_2]Br_2$.

To freshly prepared $CH_3Ge[SC(S)N(C_2H_5)_2]Cl_2$ (0.250 g, 0.81 mmol), excess $(CH_3)_3SiBr$ (1.5 mmol) and CS_2 (1 mL) were added. The solution was stirred for 2 h at ca. −20°C. The volatile materials were slowly pumped off and yellow crystals appeared. The crystals were washed with cold *n*-hexane and dried. Yield 36%, mp 62°C. Anal. Calcd for $C_6H_{13}NS_2Br_2$: C, 18.21; H, 3.31; N, 3.54. Found: C, 18.43; H, 3.40; N, 3.69.

Attempts to prepare $CH_3Ge[SC(S)N(C_2H_5)_2]I_2$ by an exchange reaction with $(CH_3)_3SiI$ resulted in a mixture which could not be identified.

Preparation of methyltris(*N*,*N*'-diethyldithiocarbamato)germane (10), $CH_3Ge[SC(S)N(C_2H_5)_2]_3$.

The germane, CH_3GeCl_3 (1 mmol) and the solvent, CS_2 (2.5 mL) were added in sequence to a dry powder of $(C_2H_5)_2NCS(S)Na$ (0.535 g, 3.12 mmol). The vessel was warmed up to ambient temperature and the color of the mixture turned yellow. The reaction mixture was stirred for 5 h before it was filtered. The filtrate on evaporation gave a yellow microcrystalline product, which was washed with cold ligroin and dried. Yield 52%, mp 94°C. Anal. Calcd for $C_{14}H_{33}N_3S_6Ge$: C, 36.10; H, 6.25; N, 7.89. Found: C, 34.23; H, 6.92; N, 8.18.

Preparation of triphenyl(*N*,*N*'-diethyldithiocarbamato)germane (11), $(C_6H_5)_3Ge[SC(S)N(C_2H_5)_2]$.

The dry salt, $(C_2H_5)_2NCS(S)Na$ (0.511 g, 2.98 mmol) and $(C_6H_5)_3GeCl$ (0.441 g, 1.30 mmol) were mixed together and the reaction vessel was evacuated. The solvent, CS_2 (3 mL) was distilled into the vessel and the contents were stirred moderately at 0°C for 10 h. The solid materials were separated by filtration and the solvent was pumped off immediately. The viscous product thus obtained was dissolved in fresh CS_2 and on slow evaporation of the solvent white crystals appeared. Yield 60%, mp 128°C. Anal. Calcd for $C_{23}H_{25}NS_2Ge$: C, 61.10; H, 5.57; N, 3.10. Found: C, 60.98; H, 5.40; N, 3.04.

Preparation of diphenylbis(*N*,*N*'-diethyldithiocarbamato)germane (12), $(C_6H_5)_2Ge[SC(S)N(C_2H_5)_2]_2$.

The germane, $(C_6H_5)_2GeCl_2$ (0.332 g, 1.12 mmol) was dissolved in CS_2 (3 mL) and the solution was added to dry $(C_2H_5)_2NCS(S)Na$ (0.507 g, 2.96 mmol) under nitrogen atmosphere. The reaction mixture was immediately frozen by liquid nitrogen (−196°C) and the reaction vessel was evacuated. The contents were allowed to warm up to ambient temperature and were stirred moderately for 4 h. The mixture was filtered, and the filtrate on evaporation yielded a solid product, which was recrystallized from CS_2 and *n*-hexane. Yield 72%, mp 144°C. Anal. Calcd for $C_{22}H_{30}N_2S_4Ge$: C, 50.49; H, 5.78; N,5.35. Found: C, 50.79; H, 5.66; N, 5.38.

Attempted preparation of phenyltris(*N*,*N*'-diethyldithiocarbamato)-germane, $C_6H_5Ge[SC(S)N(C_2H_5)_2]_3$ and the intermediate compounds, $C_6H_5Ge[SC(S)N(C_2H_5)_2]_xCl_{3-x}$.

Excess salt, $(C_2H_5)_2NCS(S)Na$ was used with $C_6H_5GeCl_3$ in CS_2. Viscous hygroscopic products were obtained, which could not be characterized.

The compounds (1 - 12) outlined in Scheme 1 and 2 are susceptible to moisture and air. The intermediate partially substituted halo compounds are especially sensitive, and cannot be stored for a long period of time. The compounds dissolve well in common organic solvents, such as CS_2 and $CHCl_3$, and on heating, have a general tendency to sublime. It is essential to maintain moisture free conditions during the reactions, otherwise hydrolysis occurs and the alkylammonium salt of dithiocarbamic acid as well as oxides of germanes are obtained, such as:

$$2\ Me_3GeBr + 2\ NaS\overset{S}{\overset{\|}{C}}NMe_2 + H_2O \longrightarrow [Me_2NH_2][S\overset{S}{\overset{\|}{C}}NMe_2] + [Me_3Ge]_2O + CS_2 + 2\ NaBr$$

$$3\ Ph_2GeCl_2 + 6\ NaS\overset{S}{\overset{\|}{C}}NMe_2 + 3\ H_2O \longrightarrow 3[Me_2NH_2][S\overset{S}{\overset{\|}{C}}NMe_2] + [Ph_2GeO]_3 + 3\ CS_2 + 6\ NaCl$$

The above reactions were followed by ^1H nmr spectroscopy. The formation of the ammonium salt, $(CH_3)_2NH_2[SC(S)N(CH_3)_2]$,[64] and the trimeric germanium oxide, $[(C_6H_5)_2GeO]_3$[65] were confirmed

by X-ray crystallography. The structural data were identical to those previously reported.

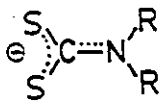
Particularly interesting is the observation of a change in the ratios of mono and bis species in the reaction of $(CH_3)_2GeCl_2$ and $Na[SC(S)N(CH_3)_2]$ with time. However, the reaction of $(CH_3)_2Cl_2$ and $Na[SC(S)N(C_2H_5)_2]$ produces only the monosubstituted derivative. The situation is reversed in the reactions involving $(C_6H_5)_2GeCl_2$.

Scrambling equilibria between halosilanes and halogermanes have been investigated in detail.[66,67] In contrast, the exchange reactions involving organogermanium dithiocarbamates clearly favor the formation of the heavier germanium-halogen bond, with no mixed halogen species being produced.

CHAPTER V

THE CHARACTERIZATION OF ORGANOGERMANIUM DITHIOCARBAMATES

The differentiation between various possible bonding modes for $SC(S)NR_2$ ligands has been the centerpiece of extensive spectroscopic studies. The structure of the dithiocarbamate group may be represented as:



The extent of the double bond character of the carbon-nitrogen bond depends on the electron releasing ability of the alkyl groups, and the nature of the metal involved. Detailed vibrational studies of a large number of dithiocarbamates have been carried out, the major aspect being the position of the ν(C-N) stretch, which lies intermediate between ν(C-N) (ca. 1250 cm^{-1}) and ν(C=N) (ca. 1600 cm^{-1}) stretches.[30] The existence of this band has also been confirmed by the normal coordinate analysis of $Pt[SC(S)NH_2]$.[48] The position of the ν(C-N) stretch and that of ν(C=S) have been utilized to predict the nature of the dithiocarbamate group. In dithiocarbamic acid esters, which can be considered as monodentate dithiocarbamates, the ν(C=S) band appears as a broad feature rather than as a sharp band. A high value for the ν(C-N) stretch close to that for a ν(C=N) stretch at ca. 1600 cm^{-1}, and a single band for the ν(C=S) band around 1000 cm^{-1} are usually seen in compounds containing a bidentate dithiocarbamate group, while a ν(C-N) band around 1485 cm^{-1} along with two ν(C=S) bands indicates a monodentate link.[29]

In the ^1H nmr spectra the chemical shifts of the substituents on nitrogen may be indicative of the bonding mode of the dithiocarbamate group. For example, a monodentate dithiocarbamate group, as in an ester, should have an N-C$\underline{H}_3$ signal at ca. 3.4 ppm.[69] Tin dithiocarbamates,[29] which are essentially monodentate have N-C$\underline{H}_3$ signals at ca. 3.4 ppm. A bidentate dithiocarbamate group, as in $Na[SC(S)N(CH_3)_2]$, should have the resonance at ca. 3.8 ppm. Features in the nmr spectra have been used in the cases of mixed ligand dithiocarbamates[70,71] to distinguish between the bonding modes of the dithiocarbamate groups. However, these values should be interpreted along with other spectroscopic data. Fluxional behaviour of dithiocarbamate complexes has been observed in titanium[55] and molybdenum compounds.[72]

Attempts have been made to relate the values of the $\underline{C}$=S chemical shifts in $^{13}C\{^1H\}$ nmr spectra to the nature of the bonding in the dithiocarbamates.[73] In $Ni[SC(S)N(C_2H_5)_2]_2$ the ligands are bidentate[74] and the $\underline{C}$=S chemical shift is at 206.4 ppm, whereas in $Ir[SC(S)N(C_2H_5)_2]_3(C_8H_{12})$ there is one bidentate as well as two monodentate ligands and the values are 205.0, 196.3 and 191.7 ppm.[75]

The (*N*,*N*'-dialkyldithiocarbamato)germanes (1 - 12) were characterized by ^1H nmr and $^{13}C\{^1H\}$ nmr, ir and Raman spectroscopy and mass spectrometry. Because the compounds are susceptible to moisture and air, they were freshly prepared on several occasions for different characterizations. The ir

spectra were recorded in an air-tight device and the Raman spectra were recorded in sealed capillary tubes. For ^{13}C nmr spectra, a relatively large quantity of sample (ca. 50 mg) and a long delay time (2 s) were required to observe the thiocarbonyl resonance.

V.1 ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra

The ^{1}H nmr spectra of the compounds (1 to 12) are illustrated in Figures 3 to 10 and the chemical shifts are presented in Tables 1 and 2. The $^{13}C\{^{1}H\}$ nmr spectra are illustrated in Figures 11 and 12, and the chemical shifts are presented in Tables 3 and 4. The ^{1}H nmr spectra of *N,N'*-dimethyldithiocarbamic acid derivatives of methylgermanes consist of two sharp singlets attributable to the N-CH_3 and Ge-CH_3 groups. The spectra of *N,N'*-diethyldithiocarbamic acid derivatives show a quartet and a triplet assignable to the N-C_2H_5 group and a sharp singlet due to the Ge-CH_3 groups. The phenylgermane derivatives display two sets of multiplets as opposed to a single set of multilplets observed in $(C_6H_5)_3GeCl$ and $(C_6H_5)_2GeCl_2$. The chemical shifts of both N-CH_3 (ca. 3.40 ppm) and N-C_2H_5 (ca. 3.75 and 1.25 ppm) groups are relatively insensitive to substitution and do not change significantly from compound to compound. Similar chemical shifts are observed in analogous tin compounds.[29] Interestingly, the triphenyl(*N,N'*-dimethyldithiocarbamato)germane (5), displays two separate signals for N-CH_3 groups, similar to those observed in the ^{1}H nmr

spectrum of *N,N'*-dimethylformamide. Although, this is observed only for one compound, the non-equivalence of the N-CH_3 groups is not entirely unexpected in view of the symmetry of the molecule and the restricted rotation of the N-CH_3 substituent. In mixed ligand dithiocarbamates of molybdenum and tungsten similar effects have been noted.[74]

In contrast to the insensitivity demonstrated by the N-CH_3 and the N-C_2H_5 groups, the Ge-CH_3 signals vary over a wide range, their positions being determined by the number of halogen atoms and dithiocarbamate moieties attached. The Ge-CH_3 resonance of trimethyl(*N,N'*-dimethyldithiocarbamato)germane (1) and trimethyl-(*N,N'*-diethyldithiocarbamato)germane (2) appear at 0.67 and 0.65 ppm respectively, which are close to that of $(CH_3)_3GeSCH_3$ at 0.51 ppm.[77] However, the Ge-CH_3 signal of $(CH_3)_2Ge(SCH_3)_2$ at 0.74 ppm[78] differs substantially from that of dimethylbis(*N,N'*-dimethyldithiocarbamato)germane (3) which resonates at 1.37 ppm. The shift of approximately 0.7 ppm per dithiocarbamate group replacing a methyl group is close to that observed for the sequential replacement by a halogen atom, as shown by $(CH_3)_4Ge$ (0.13 ppm) - $(CH_3)_3GeCl$ (0.78 ppm) - $(CH_3)_3GeBr$ (0.88 ppm) - $(CH_3)_3GeI$ (0.98 ppm)[79] shifting to $(CH_3)_2GeCl_2$ (1.18 ppm) - $(CH_3)_2GeBr_2$ (1.46 ppm) - $(CH_3)_2GeI_2$ (1.90 ppm).[80] In fact, the effect of the dithiocarbamate group can be described as that expected for substitution of a large halogen atom with an electronegativity close to that of bromine. Thus, the Ge-CH_3 shifts are 1.42 and 1.34 ppm for chlorodimethyl(*N,N'*-dimethyl-

dithiocarbamato)germane (2) and chlorodimethyl(*N*,*N*'-diethyldithiocarbamato)germane (8) respectively, comparable to 1.34 ppm for $(CH_3)_2GeBrCl$.[44] Similarly, the chemical shift of $(CH_3)_2GeBr_2$ at 1.46 ppm is almost identical to those of bromodimethyl(*N*,*N*'-dimethyldithiocarbamato)germane (2a) at 1.47 ppm and bromodimethyl(*N*,*N*'-diethyldithiocarbamato)germane (8a) at 1.50 ppm. The Ge-CH_3 resonance of $(CH_3)_2GeBrI$ is 1.65 ppm, which is close to 1.68 ppm in iododimethyl(*N*,*N*'-dimethyldithiocarbamato)-germane (2b), and 1.72 ppm in iododimethyl(*N*,*N*'-diethyldithiocarbamato)germane (8b). The same comparisons can be extended to dihalomethyldithiocarbamates as well. The Ge-CH_3 values for dichloromethyl(*N*,*N*'-dimethyldithiocarbamato)germane (4) and dichloromethyl(*N*,*N*'-diethyldithiocarbamato)germane (9) are 1.84 ppm and 1.88 ppm respectively compared to 1.74 ppm for CH_3GeCl_2Br.[47] Compared to the Ge-CH_3 chemical shift of 2.02 ppm for CH_3GeBr_3, the values for dibromomethyl(*N*,*N*'-dimethyldithiocarbamato)germane (4a) at 2.12 ppm, dibromomethyl(*N*,*N*'-diethyldithiocarbamato)germane (9a) at 2.17 ppm and methyltris(*N*,*N*'-diethyldithiocarbamato)germane (10) at 1.93 ppm are remarkably close.

The ^{13}C nmr chemical shifts of compounds (1 - 12) have similar characteristics to those observed in the case of the ^1H nmr spectra. The N-CH_3 (ca. 44 ppm) and N-C_2H_5 (ca. 49 and 12 ppm) signals virtually remain in the same positions. The chemical shifts of the Ge-C_6H_5 signals for phenylgermanium derivatives lie between 128.1 and 139.2 ppm, which are very

similar to those of $(C_6H_5)_3GeCl$ and $(C_6H_5)_2GeCl_2$. The comparison that the dithiocarbamate groups have a similar effect to that of the bromine atom can be further extended to the ^{13}C nmr chemical shifts of Ge–$\underline{C}H_3$ groups. The ^{13}C nmr signals of $(CH_3)_3GeBr$, $(CH_3)_2GeBr_2$ and CH_3GeBr_3 appear at 5.1, 15.1 and 20.4 ppm respectively.[81] Thus, the chemical shift of the Ge–$\underline{C}H_3$ group in bromodimethyl(*N*,*N*'–dimethyldithiocarbamato)germane (2a) at 16.5 ppm and that of bromodimethyl(*N*,*N*'–diethyldithiocarbamato)germane (8a) at 17.2 ppm are reasonably close to that of $(CH_3)_2GeBr_2$. A glance at Tables 3 and 4 clearly shows the similar effects that bromine and dithiocarbamate groups have on Ge–$\underline{C}H_3$ chemical shifts.

The $\underline{C}$=S chemical shifts for the methylgermanium dithiocarbamates lie in the range of 190.2 to 198.7 ppm, suggesting that none should contain truly bidentate dithiocarbamate groups. Similar $\underline{C}$=S chemical shifts are observed for tin and arsenic dithiocarbamates in which the bonding mode is anisobidentate.[73]

V.2 Infrared and Raman Spectra

The vibrational data of the dithiocarbamate compounds are given in Tables 5 to 12, and the infrared spectra along with some Raman spectra are shown in Figures 13 to 22. The typical CH_3 and CH_2 modes, such as the $\nu(CH_3–N)$ and $\nu(CH_3–Ge)$ stretching vibrations, occur in the 3000 – 2800 cm^{-1} region, their rocking and wagging modes around 1130 cm^{-1} and the distinctive $\rho(CH_3–Ge)$

rocking modes around 840 cm^{-1}. Of the six metal sensitive phenyl vibrations,[82] those four occurring in the mid-infrared region (1090, 695, 460 and 330 cm^{-1}) are readily identifiable, as their positions are not significantly influenced by the dithiocarbamate groups. The stretching bands arising from the dithiocarbamate group are remarkably similar to those observed in analogous tin compounds.[28,29] The position of the ν(C-N) band for the germanium dithiocarbamates in the range of 1579 - 1487 cm^{-1} overlaps the high energy end of the monodentate bonding region.[30] However, the presence of a single band for ν(C=S) around 970 cm^{-1} seems to support the occurence of a bidentate linkage. This apparently conflicting data correlates well with tin analogues which have, dithiocarbamate ligands which are neither truly monodentate nor bidentate.

The ν(Ge-C) asymmetric and symmetric stretching modes of methylgermanium dithiocarbamates, in the 635 - 560 cm^{-1} region, are very similar to those of the parent germanes. For example, in the infrared spectra of $(CH_3)_3GeBr$ the ν(Ge-C) asymmetric and symmetric stretching vibrations appear at 612 and 572 cm^{-1} compared to 610 and 569 for trimethyl(*N*,*N*'-dimethyldithiocarbamato)germane (1), and those of $(CH_3)_2GeBr_2$ appear at 633 and 588 cm^{-1} compared to 629 and 578 cm^{-1} for dimethyl(*N*,*N*'-dimethyldithiocarbamato)germane (3).[83] The presence of the symmetric stretching bands of medium intensity suggest that the C-Ge-C moiety is non-linear and a trans geometry cannot be expected.

The ν(Ge–S) vibration[86] appears in the 435 – 400 cm^{-1} region, similar to those in $(CH_3)_3GeSR$[85] and the band often overlaps the $\delta(CS_2)$ mode of the dithiocarbamate group.

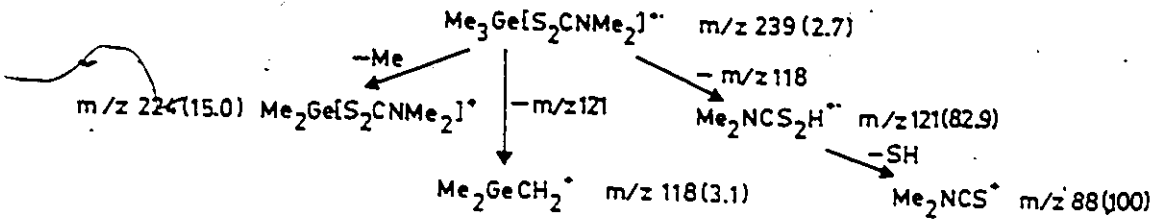
Interestingly, the ν(Ge–Cl) stretch of chlorodimethyl(*N*,*N*'-dimethyldithioicarbamato)germane occurs at 321 cm^{-1} (310 cm^{-1} Raman) which is approximately 100 cm^{-1} lower than that of a normal ν(Ge–Cl) vibration as observed in $(CH_3)_3GeCl$ (399 cm^{-1})[84] or $(CH_3)_2GeCl_2$ (410 cm^{-1}).[87,88] The bromo or iodo analogues do not have any band around 321 cm^{-1}, clearly indicating that the nature of the Ge–Cl bond has changed on formation of the dithiocarbamate. Similarly, the ν(Ge–Br) and ν(Ge–I) bands for these compounds were observed in the Raman spectra at 202 and 137 cm^{-1} respectively, which are considerably lower than normal ν(Ge–Br) (ca. 279 cm^{-1})[83] and ν(Ge–I) (ca. 231 cm^{-1})[89] bands. In chlorodimethyl(*N*,*N*'-diethyldithiocarbamato)germane (8), the value of the ν(Ge–Cl) stretch is 285 cm^{-1} and similarly lower values for bromo and iodo analogues were obtained. This suggests that all these intermediate compounds have similar structures which might be related to the long pseudo-axial Ge–Cl bond, found in $Cl_3Ge.N(CH_3)_3$,[90,91] which is the only other compound in which a ν(Ge–Cl) stretch has been reported in the 300 cm^{-1} range.

In the ν(Ge–C) stretching region of dihalomethyldithiocarbamates there should obviously be one peak corresponding to the single methyl group attached to germanium. The bands around 600 cm^{-1} clearly belong to the ν(Ge–C) stretch.[92] However, the band around 595 cm^{-1} observed for all of the compounds defies

simple explanation, since this band is absent in the dithiocarbamate salts. The prominent bands around 380 cm^{-1} and 271 cm^{-1} suggest the presence of normal ν(Ge-Cl) and ν(Ge-Br) stretches. However, weak bands around 300 cm^{-1} and 220 cm^{-1} suggest the possibility of weak Ge-X bonds, which are presumably due to axial halogens.

V.3 Mass Spectra

The mass spectral data are summarized in Tables 13 to 20 and two typical spectra are shown in Figures 23 and 24. A representative fragmentation pattern is shown below.



The germanium isotope pattern is evident in all clusters containing germanium and are clearly discernible from other fragments. The molecular ions are observed from all the compounds and in essence, the fragmentation pattern of the dithiocarbamates are reminiscent of those of corresponding halomethyl and halophenylgermanes.[13] The complex patterns of peaks containing germanium, halogen and sulfur were compared to theoretical patterns thus adding confirmation of the assignments

of ions. The free acid peaks are present in all the compounds, and interestingly, they are also observed in corresponding esters[74] and dialkylammonium salts. Fragmentation patterns for the germanium dithiocarbamates also involve the loss of methyl, phenyl, CS_2 and CS, and are similar to those found in a number of metal dithiocarbamates.[75] Particularly interesting is the formation of free acid oligomers involving up to four molecules with loss of hydrogen and methyl groups. The abundance of these species indicate that the dithiocarbamate groups are not strongly held and that the metal–sulfur link is relatively weak.

Table 1 ^1H nmr Data of *N,N'*-Dimethyldithiocarbamic Acid Derivatives of Methyl and Phenylgermanes[a]

Compound	No.	Chemical Shifts δ in ppm[b] Ge-C<u>H</u>$_3$/C$_6$<u>H</u>$_5$	N-C<u>H</u>$_3$
$(CH_3)_3Ge[S_2CN(CH_3)_2]$	1	0.67(9H)	3.37(6H)
$(CH_3)_2Ge[S_2CN(CH_3)_2]Cl$	2	1.42(6H)	3.42(6H)
$(CH_3)_2Ge[S_2CN(CH_3)_2]Br$	2a	1.47(6H)	3.33(6H)
$(CH_3)_2Ge[S_2CN(CH_3)_2]I$	2b	1.68(6H)	3.35(6H)
$(CH_3)_2Ge[S_2CN(CH_3)_2]_2$	3	1.37(6H)	3.28(12H)
$CH_3Ge[S_2CN(CH_3)_2]Cl_2$	4	1.84(3H)	3.37(6H)
$CH_3Ge[S_2CN(CH_3)_2]Br_2$	4a	2.12(3H)	3.37(6H)
$(C_6H_5)_3Ge[S_2CN(CH_3)_2]$[c]	5	7.2 - 7.6(15H)	3.53(3H) 3.56(3H)
$(C_6H_5)_2Ge[S_2CN(CH_3)_2]Cl$[c]	6	7.3 - 7.8(10H)	3.33(6H)

[a] The N-C<u>H</u>$_3$ peak of $NaS_2CN(CH_3)_2$ in D_2O appears at 3.78 ppm.

[b] Spectra were run in CS_2.

The number of expected protons in parentheses.

[c] In $CDCl_3$.

Table 2 ^{1}H nmr Data of *N,N'*-Diethyldithiocarbamic Acid Derivatives of Methyl and Phenylgermanes[a]

Compound	No.	Chemical Shifts δ in ppm[b]		
		Ge-C<u>H</u>$_3$/C$_6$<u>H</u>$_5$	N-C<u>H</u>$_2$	C<u>H</u>$_3$
$(CH_3)_3Ge[S_2CN(C_2H_5)_2]$	7	0.65(9H)	3.80(4H, q)	1.22(6H, t)
$(CH_3)_2Ge[S_2CN(C_2H_5)_2]Cl$	8	1.34(6H)	3.72(4H, q)	1.28(6H, t)
$(CH_3)_2Ge[S_2CN(C_2H_5)_2]Br$	8a	1.50(6H)	3.75(4H, q)	1.30(6H, t)
$(CH_3)_2Ge[S_2CN(C_2H_5)_2]I$	8b	1.72(6H)	3.76(4H, q)	1.29(6H, t)
$CH_3Ge[S_2CN(C_2H_5)_2]Cl_2$	9	1.88(3H)	3.78(4H, q)	1.29(6H, t)
$CH_3Ge[S_2CN(C_2H_5)_2]Br_2$	9a	2.17(3H)	3.73(4H, q)	1.30(6H, t)
$CH_3Ge[S_2CN(C_2H_5)_2]_3$	10	1.93(3H)	3.73(12H, q)	1.30(18H, t)
$(C_6H_5)_3Ge[S_2CN(C_2H_5)_2]$	11	7.0 - 7.6(15H)	3.75(4H, q)	1.20(6H, t)
$(C_6H_5)_2Ge[S_2CN(C_2H_5)_2]_2$	12	7.1 - 7.9(10H)	3.68(8H, q)	1.15(12H, t)

[a] For $NaS_2CN(C_2H_5)$ in D_2O the N-C<u>H</u>$_2$ and C<u>H</u>$_3$ signals appear at 4.03(q, J=7 Hz) and 1.22(t, J=7 Hz) respectively.

[b] All spectra were recorded in CS_2.

The number of protons and multiplicities in parentheses.

t = triplet, q = quartet and J = the coupling constant.

Table 3 ^{13}C nmr Data of *N,N'*-Dimethyldithiocarbamic Acid Derivatives of Methyl and Phenylgermanes[a]

Compound	No.	Chemical Shifts δ in ppm[b] Ge-$\underline{C}H_3/C_6H_5$	N-$\underline{C}H_3$	$\underline{C}$=S
$(CH_3)_3Ge[S_2CN(CH_3)_2]$	1	3.2	44.4	196.9
$(CH_3)_2Ge[S_2CN(CH_3)_2]Cl$	2	14.8	43.2	195.9
$(CH_3)_2Ge[S_2CN(CH_3)_2]Br$	2a	16.5	44.3	197.1
$(CH_3)_2Ge[S_2CN(CH_3)_2]I$	2b	17.7	44.3	198.7
$(CH_3)_2Ge[S_2CN(CH_3)_2]_2$[c]	3	13.7	43.8	198.5
$CH_3Ge[S_2CN(CH_3)_2]Cl_2$	4	24.7	45.1	193.3
$CH_3Ge[S_2CN(CH_3)_2]Br_2$	4a	27.6	44.9	193.3
$(C_6H_5)_3Ge[S_2CN(CH_3)_2]$[d]	5	128.4, 129.7, 134.4, 135.1, 136.0, 137.7	44.6	193.9
$(C_6H_5)_2Ge[S_2CN(CH_3)_2]Cl$[e]	6	128.5, 130.2, 133.6, 136.1, 139.2	44.5	194.6

[a] For $NaS_2CN(CH_3)_2$ in D_2O the N-$\underline{C}H_3$ and $\underline{C}$=S peaks appear at 47.7 and 210.5 ppm respectively downfield from $(CH_3)_3Si(CH_2)_2CO_2Na$ (TSP).

[b] All spectra were run in $CDCl_3$.

[c] In $CDCl_3/C_6D_6$.

[d] For $(\underline{C}_6H_5)_3GeCl$ the signals are 128.8, 130.6, 134.2 and 134.9.

[e] For $(\underline{C}_6H_5)_2GeCl_2$ the signals are 129.2, 131.9, 132.8 and 134.6.

Table 4 ^{13}C nmr Data of *N,N'*-Diethyldithiocarbamic Acid Derivatives of Methyl and Phenylgermanes[a]

Compound	No.	Chemical Shifts δ in ppm[b] Ge-$\underline{C}H_3/\underline{C}_6H_5$	N-$\underline{C}H_2$	$\underline{C}H_3$	$\underline{C}$=S
$(CH_3)_3Ge[S_2CN(C_2H_5)_2]$	7	3.3	48.5	12.2	195.0
$(CH_3)_2Ge[S_2CN(C_2H_5)_2]Cl$	8	15.9	49.0	12.2	194.2
$(CH_3)_2Ge[S_2CN(C_2H_5)_2]Br$	8a	17.2	49.1	12.0	195.0
$(CH_3)_2Ge[S_2CN(C_2H_5)_2]I$	8b	18.6	49.3	12.4	196.7
$CH_3Ge[S_2CN(C_2H_5)_2]Cl_2$	9	25.8	50.0	12.1	190.2
$CH_3Ge[S_2CN(C_2H_5)_2]Br_2$	9a	28.6	49.9	12.1	191.3
$CH_3Ge[S_2CN(C_2H_5)_2]_3$	10	24.4	49.3	11.9	192.6
$(C_6H_5)_3Ge[S_2CN(C_2H_5)_2]$	11	128.3, 129.5, 134.2, 135.0, 136.2	48.9	12.6	192.0
$(C_6H_5)_2Ge[S_2CN(C_2H_5)_2]_2$	12	128.1, 129.4, 134.2, 136.6, 138.1	48.7	12.5	193.0

[a] For $NaS_2CN(C_2H_5)_2$ in D_2O the N-$\underline{C}H_2$, $\underline{C}H_3$ and $\underline{C}$=S peaks appear at 49.3, 12.3 and 207.3 ppm respectively in reference to dioxane (67.4 ppm).

[b] All spectra were run in $CDCl_3$.

Table 5 Vibrational Data[a] of $(CH_3)_3Ge[S_2CN(CH_3)_2]$ (1) and $(CH_3)_2Ge[S_2CN(CH_3)_2]_2$ (3)

Compound 1		Compound 2		Assignment
IR (neat)	Raman	IR (CCl_4)	Raman (cm^{-1})	
2971m	2969(19)	2974w	2988(17)	ν(C-H)
2912s	2903(65)	2931w	2919(70)	
2798w	2788(15)	2857w		
		(CsI)		
1494s		1501s		ν(C-N)
1403sh		1434sh		
1370s	1368(16)	1378s	1373(33)	
1249s	1239(16)	1253s	1240(10)	ν(CS_2)as
1138s		1144s		ν(C-N)
1049w		1050w		
992s	984(19)	989s	987(37)	ν(CS_2)sym
		876sh		
833sbr		832sbr		
610m	601(29)	629m	423(18)	ν(Ge-C)as
569m	563(100)	578m	571(100)	ν(Ge-C)sym
450m	452(19)	447sh	452(28)	
435m	432(19)	438mbr	429(13)	ν(Ge-S)
404w	398(34)	392w	408(35)	δ(CS_2)

a s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad. Raman intensities in parentheses.

Table 6 Vibrational Data of $(CH_3)_2Ge[S_2CN(CH_3)_2]Cl$ (2), $(CH_3)_2Ge[S_2CN(CH_3)_2]Br$ (2a) and $(CH_3)_2Ge[S_2CN(CH_3)_2]I$ (2b)

Compound 2		Compound 2a		Compound 2b		Assignment
IR	Raman	IR	Raman	IR	Raman (cm^{-1})	
(CCl_4)		(CsI)		(CsI)		
3010sh	2995(13)	3004w	2995(19)	3000m	2990(17)	ν(C-H)
2928m	2915(100)	2945m	2920(100)	2923w	2910(100)	
2859w				2872w		
(CsI)						
1521s		1532s		1536s		ν(C-N)
1458w				1459sh		
1394s	1387(17)	1399s	1386(35)	1398s	1390(31)	
1250s	1227(13)	1250s	1228(15)	1244s	1222(12)	ν(CS_2)as
1155m		1163m	1154(7)	1156s		ν(C-N)
1054w		1054w		1049w		
990s	981(26)	987s	984(29)	980s	979(23)	ν(CS_2)sym
833vsbr		835vsbr		836vsbr		
632m	622(28)	634m	631(24)	633m	627(10)	ν(Ge-C)sym
578m	572(59)	580m	582(84)	573m	576(43)	ν(Ge-C)as
453m	443(23)	449sh	447(42)	439sh	443(16)	
424m	424(25)	421sh	424(41)	409sh	409(13)	ν(Ge-S)
377sh		363vw		363vw		δ(CS_2)
321s	310(52)					ν(Ge-Cl)
			202(100)			ν(Ge-Br)
					137(36)	ν(Ge-I)

Table 7 Vibrational Data of $CH_3Ge[S_2CN(CH_3)_2]Cl_2$ (4) and $CH_3Ge[S_2CN(CH_3)_2]Br_2$ (4a)

Compound 4		Compound 4a		Assignment
IR (CsI)	Raman	IR (CCl_4)	Raman (cm^{-1})	
2985s	3005(11)	2930s	2995(18)	ν(C-H)
2866sh	2915(71)		2912(99)	
2770m		2752m		
		(CsI)		
1518vs	1548(21)	1565vs	1541(22)	ν(C-N)
1465w		1459w	1447(16)	
1401m	1388(37)	1403s	1392(56)	
1249m	1242(13)	1245m	1220(16)	$\nu(CS_2)$as
1158w		1165m	1151(9)	ν(C-N)
1054vw		1049w	1055(22)	
987w	981(21)	981w	977(32)	$\nu(CS_2)$sym
879sh		882sh		
793sbr		816mbr		
		726w	734(22)	
631w	615(75)	609w	602(100)	ν(Ge-C)
571w	569(66)	567w	568(54)	
	447(51)	441sh	444(46)	
400s	387(100)	407m		ν(Ge-S)
		286w	271(6)	ν(Ge-Br)

Table 8 Vibrational Data of $(C_6H_5)_3Ge[S_2CN(CH_3)_2]$ (5) and $(C_6H_5)_2Ge[S_2CN(CH_3)_2]_2$ (6)

Compound 5		Compound 6		Assignment
IR (CCl_4)	Raman	IR (CsI)	Raman (cm^{-1})	
3059w	3044(18)		3058(38)	
2926s	2933(11)	2964m	2926(20)	
2856m		2909w		
1579vw	1579(25)	1563sh	1576(28)	
1511vs		1516m	1526(10)	ν(C-N)
1413m			1404(13)	
1372s	1372(12)	1381w	1390(14)	
1249m		1260s		$\nu(CS_2)$ as
1148m	1153(8)		1179(16)	ν(C-N)
1089m	1084(9)	1097vs		
	1022(21)	1026vs	1021(21)	$\nu(CS_2)$ sym
984s	995(100)		996(100)	$\nu(Ge-C_6H_5)$
(Nujol)		805vs		
735s		737w		
696s	663(22)	694m	666(15)	
	616(13)		612(14)	
574w	571(17)	577w	577(35)	
461s	452(13)	461w	451(24)	
411w	409(16)	393m	427(13)	ν(Ge-S)
325m		344w		
284m		284w	291(35)	

Table 9 Vibrational Data of $(CH_3)_3Ge[S_2CN(C_2H_5)_2]$ (7) and $CH_3Ge[S_2CN(C_2H_5)_2]_3$ (10)

Compound 7		Compound 10		Assignment
IR (Neat)	Raman	IR (CsI)	Raman (cm^{-1})	
2976s	2970(12)	2981s	2974(40)	ν(C-H)
2932m	2929(18)	2949sh	2934(46)	
2906m	2904(65)		2925(33)	
2873sh		2880m		
1519w		1517vs	1533(70)	ν(C-N)
1483s	1480(10)		1487(32)	
1458m	1449(8)	1465m	1456(23)	
1438sh			1439(39)	
1414s	1409(7)	1401w	1419(28)	
1357m		1363sh	1357(21)	
1267s	1263(12)	1263m	1281(60)	$\nu(CS_2)$as
1208s		1210m		
1139s		1159sh	1141(23)	ν(C-N)
1075m	1078(8)			
1068sh	1055(19)	1069w	1076(25)	
1011m	1010(25)		1007(56)	
990m		988m	985(42)	$\nu(CS_2)$sym
919m	915(7)	910sbr	916(30)	
829sbr		840m		$\rho(Ge-CH_3)$
	734(19)	777sbr		

Table 9 continued

Compound 7		Compound 10		Assignment
IR	Raman	IR	Raman (cm^{-1})	
	659(49)	633w	653(37)	
605m	599(13)		608(58)	ν(Ge–C)as
567m	562(100)	565w	566(100)	ν(Ge–C)sym
	527(31)	514w		
473w			449(52)	
436m	420(27)	426w	408(86)	ν(Ge–S)
387w		398w	395(35)	$\delta(CS_2)$
	348(43)		319(28)	

Table 10 Vibrational Data of $(CH_3)_2Ge[S_2CN(C_2H_5)_2]Cl$ (8), $(CH_3)_2Ge[S_2CN(C_2H_5)_2]Br$ (8a) and $(CH_3)_2Ge[S_2CN(C_2H_5)_2]I$ (8b)

Compound 8		Compound 8a		Compound 8b		Assignment
IR (CsI)	Raman	IR (CsI)	Raman	IR (CsI)	Raman (cm^{-1})	
2982m	2979(54)	2982m	2974(47)	2975m	2978(16)	ν(C-H)
2938w	2929(12)	2901w	2928(12)		2931(15)	
	2912(91)		2911(74)		2911(62)	
1511m	1501(46)	1518s	1509(36)	1525s	1520(30)	ν(C-N)
1443m	1452(20)	1444m	1451(17)	1449m		
	1433(14)		1434(12)			
1275m	1270(36)	1276m	1272(34)	1277m	1274(42)	ν(CS_2)as
1209m		1207m		1204m		
1152m	1146(13)	1153m	1146(14)	1153m	1156(16)	ν(C-N)
1075m	1068(13)	1073m	1069(12)	1071mbr	1073(10)	
1012mbr	1007(21)	1011mbr	1002(16)	1002m	1005(9)	ν(CS_2)sym
922mbr	915(8)	920m	914(7)	917m	912(8)	
843vsbr		844sbr		841sbr		ρ($Ge-CH_3$)
638s	630(25)	637m	629(21)	635w	630(22)	ν(Ge-C)as
578s	579(100)	575s	575(100)	570m	573(100)	ν(Ge-C)sym
498w	525(17)	495w	527(18)	488vw		
412sbr	439(62)	407s	439(57)	402m	444(64)	ν(Ge-S)
293vsbr	287(29)					ν(Ge-Cl)
					138(34)	ν(Ge-I)

Table 11 Vibrational Data of $CH_3Ge[S_2CN(C_2H_5)_2]Cl_2$ (9) and $CH_3Ge[S_2CN(C_2H_5)_2]Br_2$ (9a)

Compound 9		Compound 9a		Assignment
IR (CsI)	Raman	IR (CsI)	Raman (cm^{-1})	
2989m	2982(25)	2982m	2977(33)	ν(C-H)
2945sh	2951(17)	2938m	2946(18)	
	2919(36)		2932(26)	
2887w		2887sh	2914(42)	
1525s	1524(55)	1533s	1526(41)	ν(C-N)
1449m	1455(18)	1441s	1454(13)	
1354m		1354m		
1282m	1280(64)	1284m	1277(59)	$\nu(CS_2)$as
1205s	1232(14)	1202m	1226(16)	
1154m	1156(31)	1154m	1154(10)	ν(C-N)
1077m	1077(16)	1075mbr	1066(10)	
1003m	1005(17)	1001m	1007(19)	$\nu(CS_2)$sym
918m		916w	918(13)	
837sbr		817sbr		$\rho(Ge-CH_3)$
614m	609(92)	610m	606(100)	ν(Ge-C)
570m		585m	569(32)	
	448(86)	448vw	447(69)	
409sh		404s		ν(Ge-S)
390s	380(100)			$\delta(CS_2)$
310s	310(48)			ν(Ge-Cl)
		288mbr	280(50)	ν(Ge-Br)

Table 12 Vibrational Data of $(C_6H_5)_3Ge[S_2CN(C_2H_5)_2]$ (11) and $(C_6H_5)_2Ge[S_2CN(C_2H_5)_2]_2$ (12)

Compound 11		Compound 12		Assignment
IR (CsI)	Raman	IR (CsI)	Raman (cm^{-1})	
3062m	3044(14)	3086w	3044(83)	ν(C-H)
2984m		2983m	2975(52)	
2934m	2931(10)	2943sh	2932(45)	
	1582(19)		1578(29)	
1487s		1489s	1482(43)	ν(C-N)
1426s		1423s	1421(15)	
1370m		1354m	1370(12)	
1268s		1268s	1262(38)	$\nu(CS_2)$as
1206s		1207s		
1141m		1141s	1140(16)	ν(C-N)
1089sbr		1080sh	1076(16)	
	1027(18)	1011sbr	1018(39)	$\nu(CS_2)$sym
1000sbr	1000(100)	990s	997(100)	$\nu(Ge-C_6H_5)$
915m		920m	918(18)	
833m		838w		
739s		737s	732(8)	
699s	664(19)	693s	664(12)	
570w	570(10)	571m	570(42)	
462s		461m		
433sh	420(21)	415mbr	437(79)	ν(Ge-S)
327m		339m	347(20)	

Table 13 Mass Spectral Data[a] of $(CH_3)_3Ge[S_2CN(CH_3)_2]$ (1) and $(CH_3)_2Ge[S_2CN(CH_3)_2]_2$ (3)

Compound 1 (EI)	Compound 3[b] (EI)	Fragment
	344(11.9)	$(CH_3)_2Ge[S_2CN(CH_3)_2]_2^{+\cdot}$
239(2.7)		$(CH_3)_3Ge[S_2CN(CH_3)_2]^{+\cdot}$
224(15.0)	224(30.1)	$(CH_3)_2Ge[S_2CN(CH_3)_2]^{+}$
137(4.0)		$(CH_3)_2GeSH^{+}$
121(82.9)	121(19.3)	$(CH_3)_2NCS_2H^{+\cdot}$
118(3.1)		$(CH_3)_2GeCH_2^{+}$
88(100)	88(100)	$(CH_3)_2NSC^{+}$
76(19.5)	76(14.9)	$CS_2^{+\cdot}$
	56(4.7)	$(CH_3)_2NC^{+}$
44(69.4)	44(46.7)	$CS^{+\cdot}$

a Relative abundances in parentheses.

b Non-germanium containing peaks appear at m/z 461 and 341.

Table 14 Mass Spectral Data of $(CH_3)_2Ge[S_2CN(CH_3)_2]Cl$ (2), $(CH_3)_2Ge[S_2CN(CH_3)_2]Br$ (2a) and $(CH_3)_2Ge[S_2CN(CH_3)_2]I$ (2b)

Compound 2[a] (EI)	Compound 2a[b] (FI)	Compound 2b (FI)	Fragment
	303(15.3)		$(CH_3)_2Ge[S_2CN(CH_3)_2]Br^{+\cdot}$
259(5.4)			$(CH_3)_2Ge[S_2CN(CH_3)_2]Cl^{+\cdot}$
244(10.3)			$CH_3Ge[S_2CN(CH_3)_2]Cl^{+}$
224(4.9)	224(100)	224(100)	$(CH_3)_2Ge[S_2CN(CH_3)_2]^{+}$
159(9.9)			$CH_3GeCl_2^{+}$
139(11.7)			$(CH_3)_2GeCl^{+}$

Table 14 continued

Compound 2	Compound 2a	Compound 2b	Fragment
121(27.6)	121(41)	121(41)	$(CH_3)_2NS_2H^+\cdot$
109(4.7)			$GeCl^+$
88(65.0)			$(CH_3)_2NCS^+$
	78(17.5)	78(41)	$CS_2H_2^+$
76(16.3)			$CS_2^+\cdot$
44(100)			$CS^+\cdot$

[a] Non-germanium containing peaks also seen at m/z 461 and 341.

[b] Association peak at m/z 382 due to $(CH_3)_2Ge[S_2CN(CH_3)_2]Br_2^+$.

Table 15 Mass Spectral Data of $CH_3Ge[S_2CN(CH_3)_2]Cl_2$ (4) and $CH_3Ge[S_2CN(CH_3)_2]Br_2$ (4a)

Compound 4 (FI)	Compound 4a (FI)	Fragment
	367(3.6)	$CH_3Ge[S_2CN(CH_3)_2]Br_2^+\cdot$
	288(77.6)	$CH_3Ge[S_2CN(CH_3)_2]Br^+$
279(28.9)		$CH_3Ge[S_2CN(CH_3)_2]Cl_2^+\cdot$
208(100)	208(100)	$[(CH_3)_2NCS]_2S^+\cdot$
121(15.8)	121(51.3)	$(CH_3)_2NCS_2H^+\cdot$
78(7.0)		$CS_2H_2^+\cdot$

Table 16 Mass Spectral Data of $(C_6H_5)_3Ge[S_2CN(CH_3)_2]$ (5) and $(C_6H_5)_2Ge[S_2CN(CH_3)_2]Cl$ (6)

Compound 5 (EI)	Compound 6 (EI)	Fragment
425(2.0)		$(C_6H_5)_3Ge[S_2CN(CH_3)_2]^{+\cdot}$
	383(29.8)	$(C_6H_5)_2Ge[S_2CN(CH_3)_2]Cl^{+\cdot}$
348(9.3)		$(C_6H_5)_2Ge[S_2CN(CH_3)_2]^{+}$
316(9.3)		$(C_6H_5)_2Ge[SCN(CH_3)_2]^{+\cdot}$
	306(100)	$C_6H_5Ge[S_2CN(CH_3)_2]Cl^{+}$
305(18.6)		$(C_6H_5)_3Ge^{+}$
	260(10.5)	$(C_6H_5)_2GeS^{+}$
	228(15.3)	$(C_6H_5)_2Ge^{+\cdot}$
154(100)		$(C_6H_5)_2^{+\cdot}$
151(15.9)	151(18.7)	$C_6H_5Ge^{+}$
88(16.1)		$(CH_3)_2NCS^{+}$
77(23.6)	77(13.1)	$C_6H_5^{+}$

Table 17 Mass Spectral Data of $(CH_3)_3Ge[S_2CN(C_2H_5)_2]$ (7) and $CH_3Ge[S_2CN(C_2H_5)_2]_3$ (10)

Compound 7 (EI)	Compound 10 (FI)	Fragment
	533(41)	$CH_3Ge[S_2CN(C_2H_5)_2]_3^{+\cdot}$
	518(41)	$Ge[S_2CN(C_2H_5)_2]_3^{+}$
267(21.7)		$(CH_3)_3Ge[S_2CN(C_2H_5)_2]^{+\cdot}$
	264(100)	$[(C_2H_5)_2NCS]_2S^{+\cdot}$
252(97.2)		$(CH_3)_2Ge[S_2CN(C_2H_5)_2]^{+}$

Table 17 continued

Compound 7	Compound 10	Fragment
149(40.0)	149(56.4)	$(C_2H_5)_2NCS_2H^+\cdot$
119(37.0)		$(CH_3)_3Ge^+$
116(100)		$(C_2H_5)_2NCS^+$
88(68.2)		$C_2H_5NCSH^+$
76(26.3)		$CS_2^+\cdot$
	73(21.1)	$(C_2H_5)_2NH^+\cdot$
58(41.1)		NCS^+
44(32.0)		$CS^+\cdot$

Table 18 Mass Spectral Data of $(CH_3)_2Ge[S_2CN(C_2H_5)_2]Cl$ (8), $(CH_3)_2Ge[S_2CN(C_2H_5)_2]Br$ (8a) and $(CH_3)_2Ge[S_2CN(C_2H_5)_2]I$ (8b)

Compound 8 (FI)	Compound 8a (FI)	Compound 8b (FI)	Fragment
		358(4.1)	$(CH_3)_2GeI_2^+\cdot$
	331(4.6)		$(CH_3)_2Ge[S_2CN(C_2H_5)_2]Br^+\cdot$
	296(3.8)		$[(C_2H_5)_2NCS_2]_2^+\cdot$
287(100)			$(CH_3)_2Ge[S_2CN(C_2H_5)_2]Cl^+\cdot$
252(8.9)	252(100)	252(100)	$(CH_3)_2Ge[S_2CN(C_2H_5)_2]^+$
	149(4.1)	149(7.4)	$(C_2H_5)_2NCS_2H^+\cdot$
148(1.8)			$(C_2H_5)_2NCS_2^+$

Table 19 Mass Spectral Data of $CH_3Ge[S_2CN(C_2H_5)_2]Cl_2$ (9) and $CH_3Ge[S_2CN(C_2H_5)_2]Br_2$ (9a)

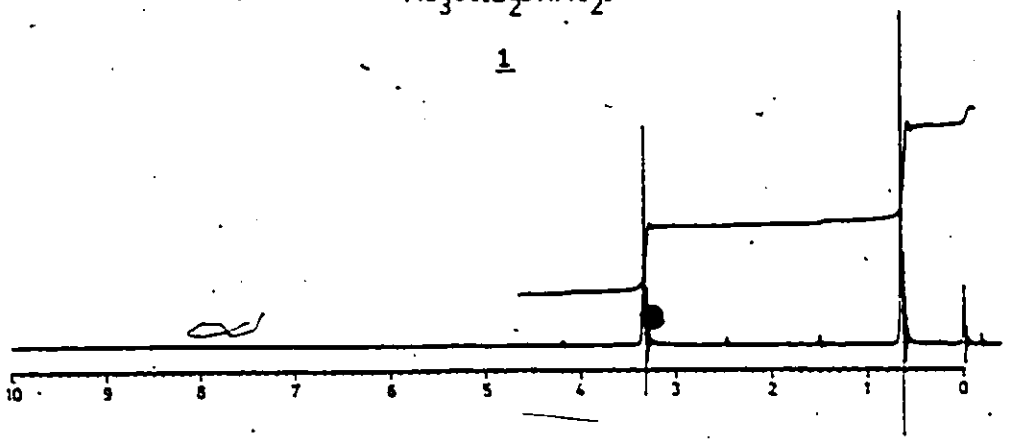
Compound 9 (FI)	Compound 9a (FI)	Fragment
	395(42.8)	$CH_3Ge[S_2CN(C_2H_5)_2]Br_2^+$
	316(87.4)	$CH_3Ge[S_2CN(C_2H_5)_2]Br^+$
307(100)		$CH_3Ge[S_2CN(C_2H_5)_2]Cl_2^+$
264(15.6)		$[(C_2H_5)_2NCS]_2S^+$
149(20.9)	149(100)	$(C_2H_5)_2NCS_2H^+$
	120(14.3)	$C_2H_5NCS_2H^+$
73(6.0)	73(23.3)	$(C_2H_5)_2NH^+$

Table 20 Mass Spectral Data of $(C_6H_5)_3Ge[S_2CN(C_2H_5)_2]$ (11) and $(C_6H_5)_2Ge[S_2CN(C_2H_5)_2]_2$ (12)

Compound 11 (FI)	Compound 12 (FI)	Fragment
453(25.2)		$(C_6H_5)_3Ge[S_2CN(C_2H_5)_2]^+$
	376(41)	$(C_6H_5)_2Ge[S_2CN(C_2H_5)_2]^+$
	296(41)	$[(C_2H_5)_2NCS_2]_2^+$
149(4.6)	149(81.0)	$(C_2H_5)_2NCS_2H^+$
120(4.9)		$C_2H_5NCS_2H^+$
73(100)	73(100)	$(C_2H_5)_2NH^+$

$Me_3Ge[S_2CNMe_2]$

1



$Me_2Ge[S_2CNMe_2]_2$

3

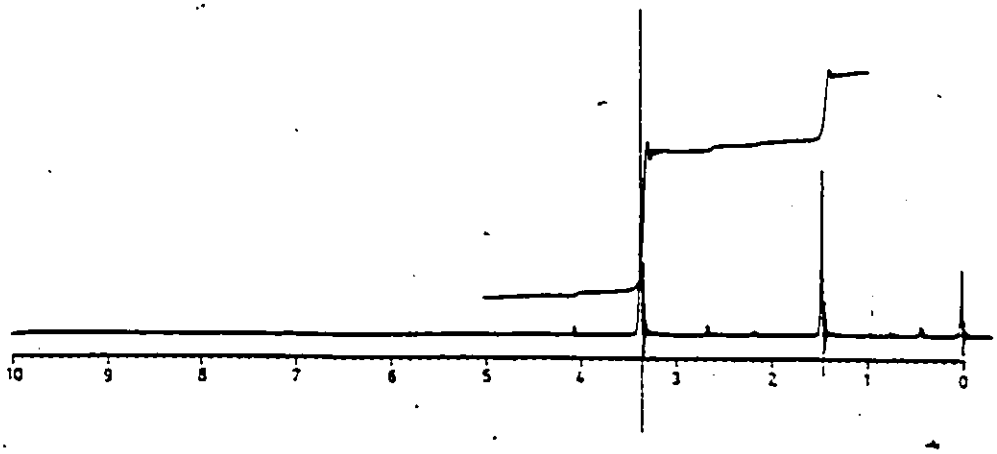
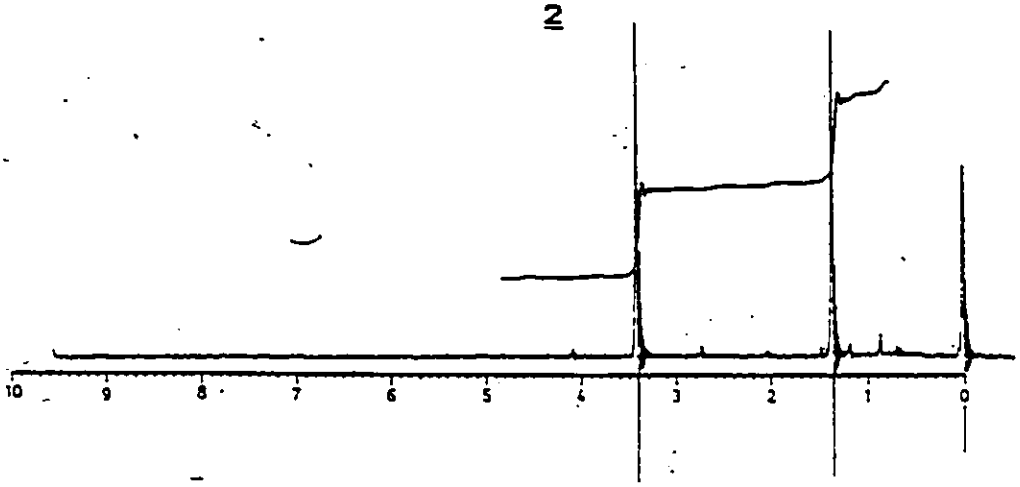


Figure 3 ^1H nmr Spectra of Compounds 1 and 3.

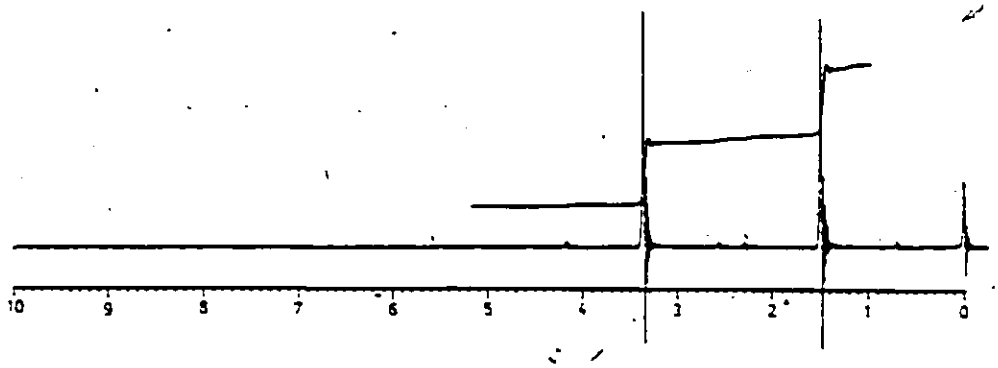
$Me_2Ge[S_2CNMe_2]Cl$

2



$Me_2Ge[S_2CNMe_2]Br$

2a



$Me_2Ge[S_2CNMe_2]I$

2b

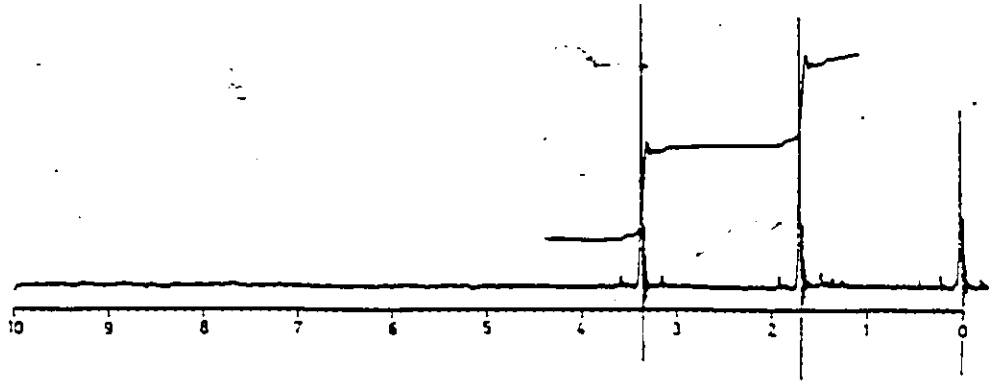
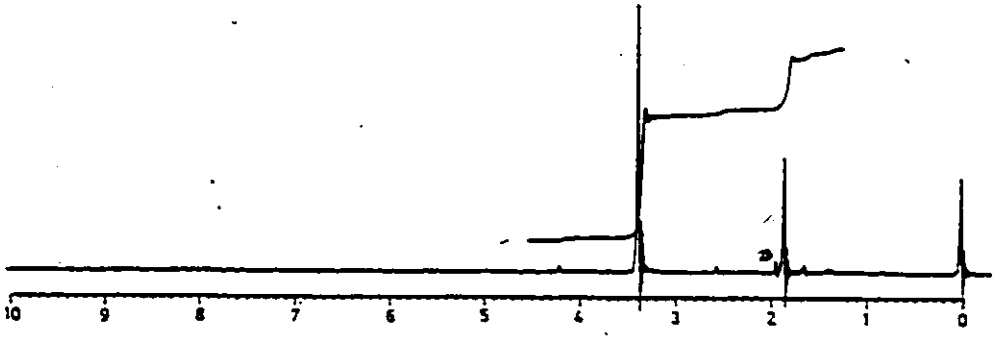


Figure 4 ^1H nmr Spectra of Compounds 2, 2a and 2b.

$MeGe[S_2CNMe_2]Cl_2$

4



$MeGe[S_2CNMe_2]Br_2$

4a

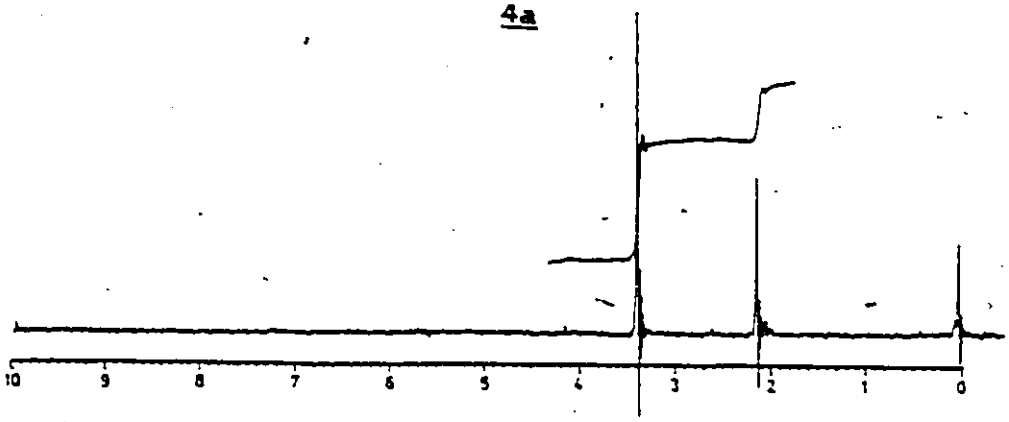


Figure 5 ^1H nmr Spectra of Compounds 4 and 4a.

$Ph_3Ge[S_2CNMe_2]$

5

$Ph_2Ge[S_2CNMe_2]Cl$

6

Figure 6 ^1H nmr Spectra of Compounds 5 and 6.

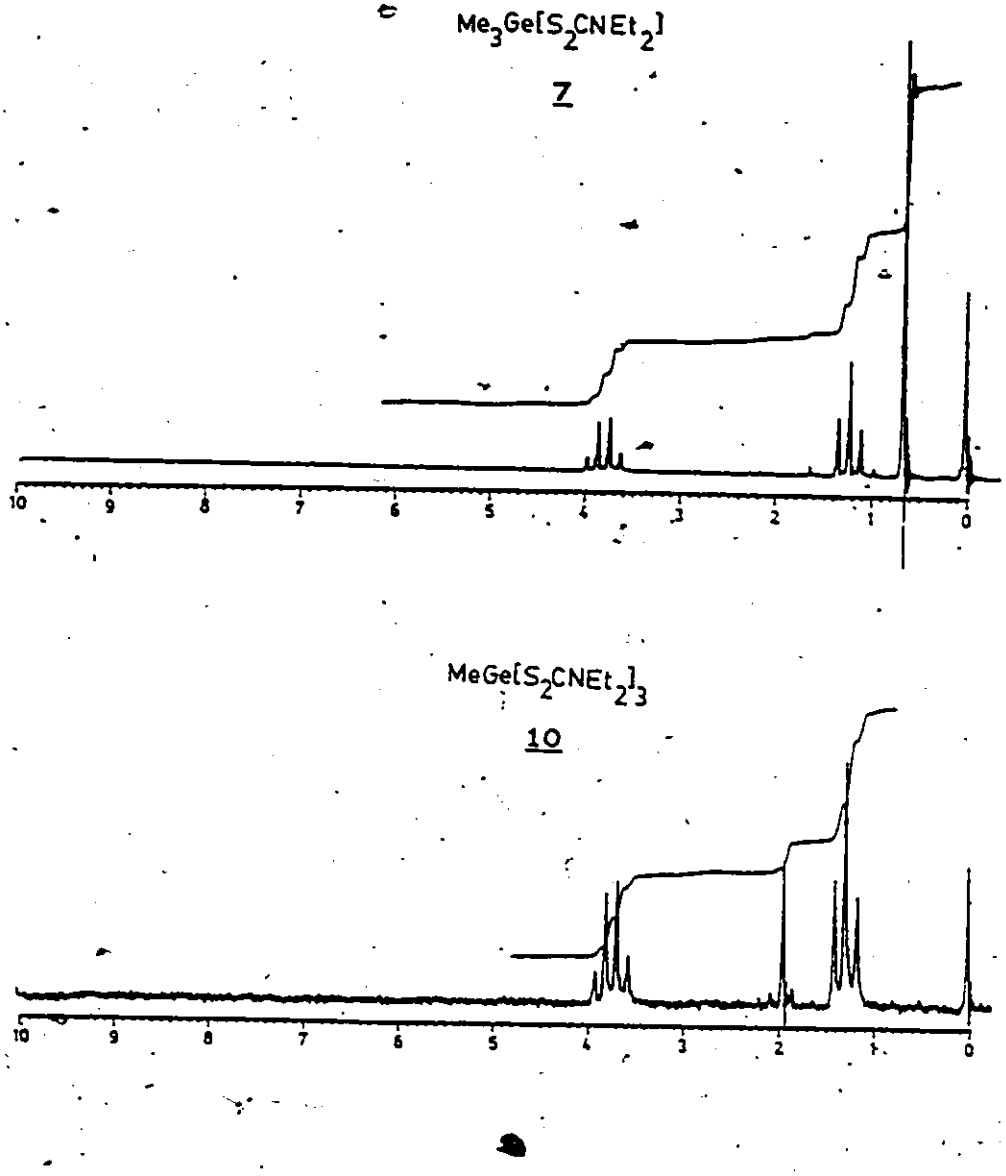


Figure 7 ^{1}H nmr Spectra of Compounds 7 and 10.

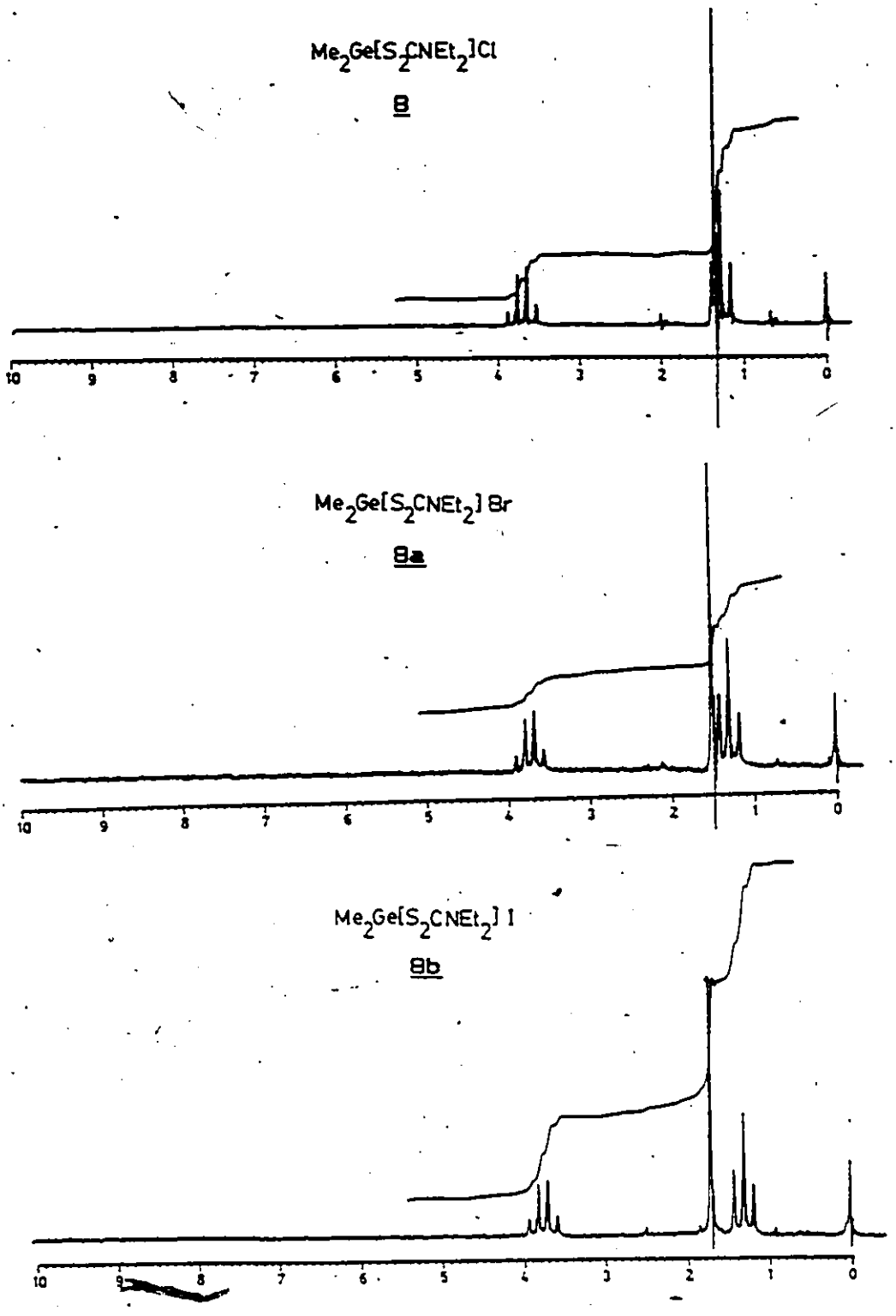


Figure 8 ^1H nmr Spectra of Compounds 8, 8a and 8b.

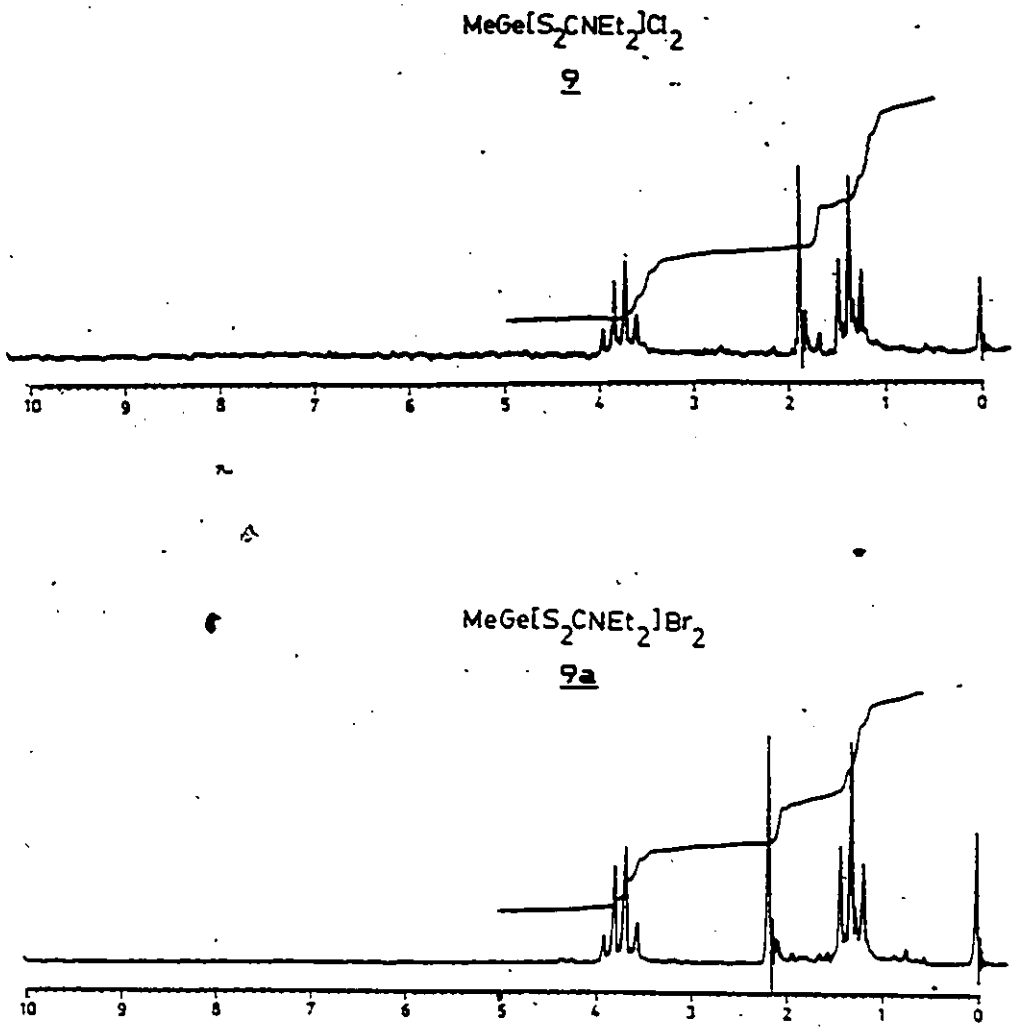


Figure 9 ^1H nmr Spectra of Compounds 9 and 9a.

$Ph_3Ge[S_2CNEt_2]$

11

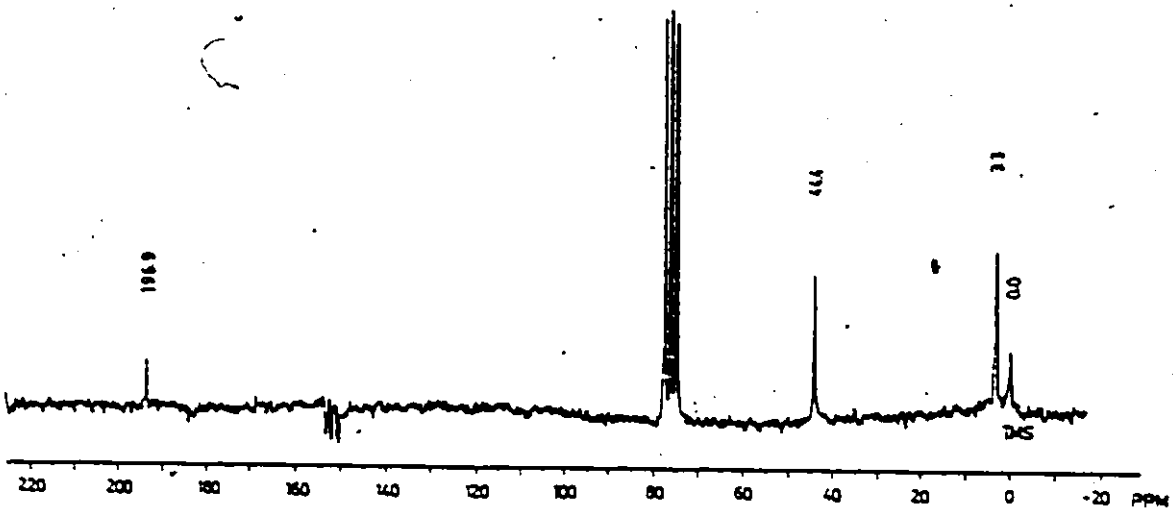
$Ph_2Ge[S_2CNEt_2]_2$

12

Figure 10 ^1H nmr Spectra of Compounds 11 and 12.

$Me_3Ge[S_2CNMe_2]$

1



$Ph_2Ge[S_2CNMe_2]Cl$

6

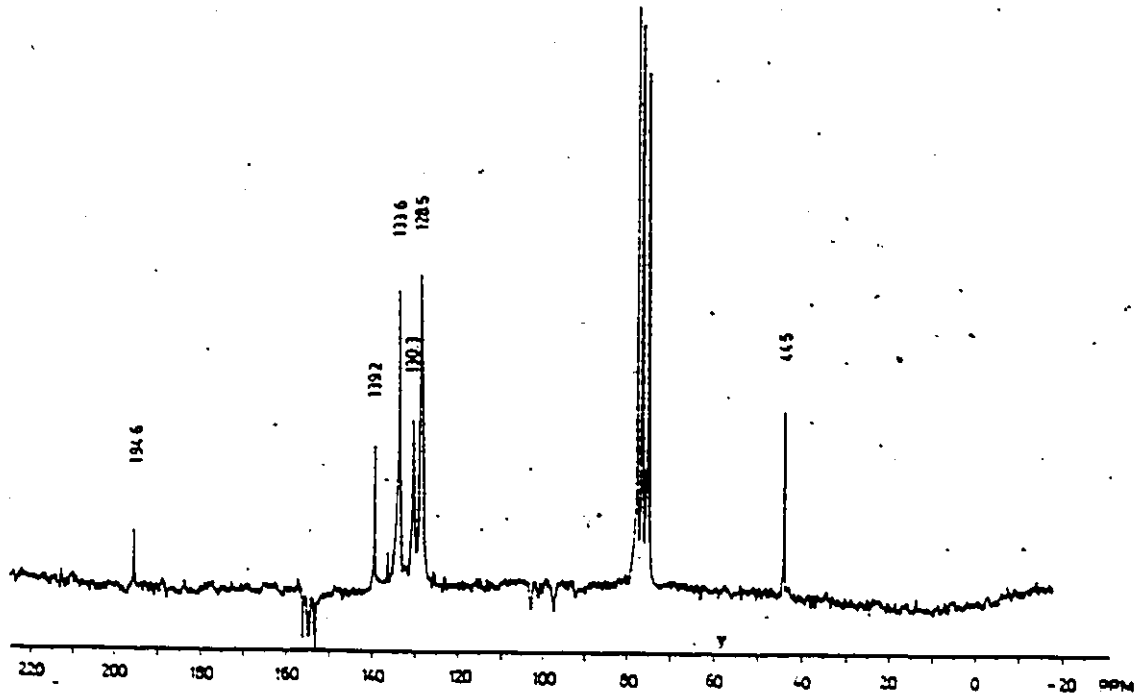


Figure 11 ^{13}C nmr Spectra of Compounds 1 and 6.

$MeGe[S_2CNEt_2]Cl_2$

9

$Ph_3Ge[S_2CNEt_2]$

11

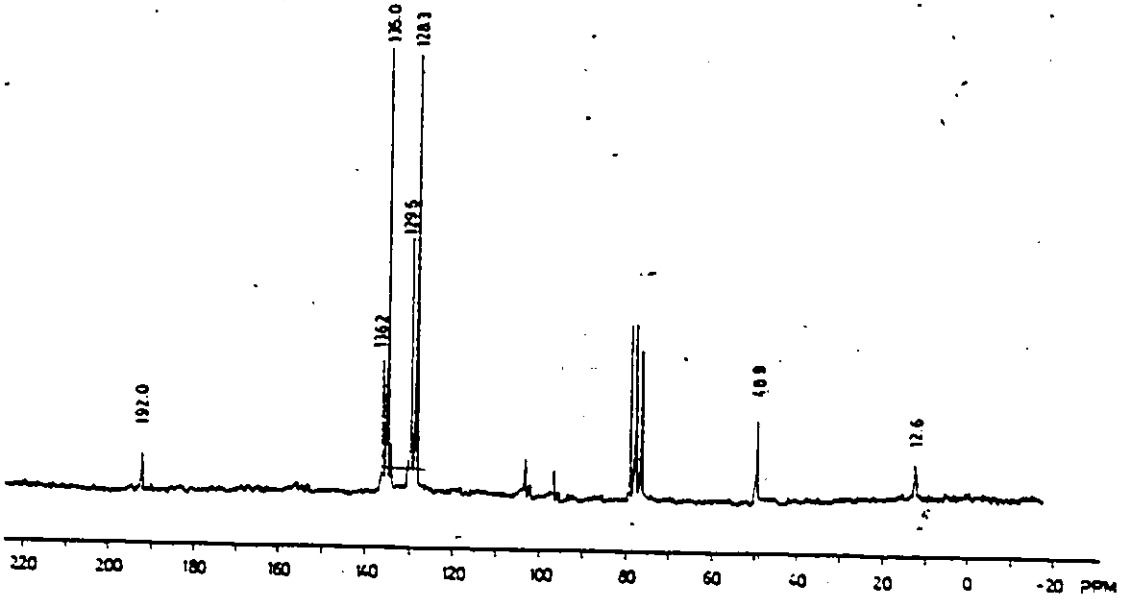


Figure 12 ^{13}C nmr Spectra of Compounds 9 and 11.

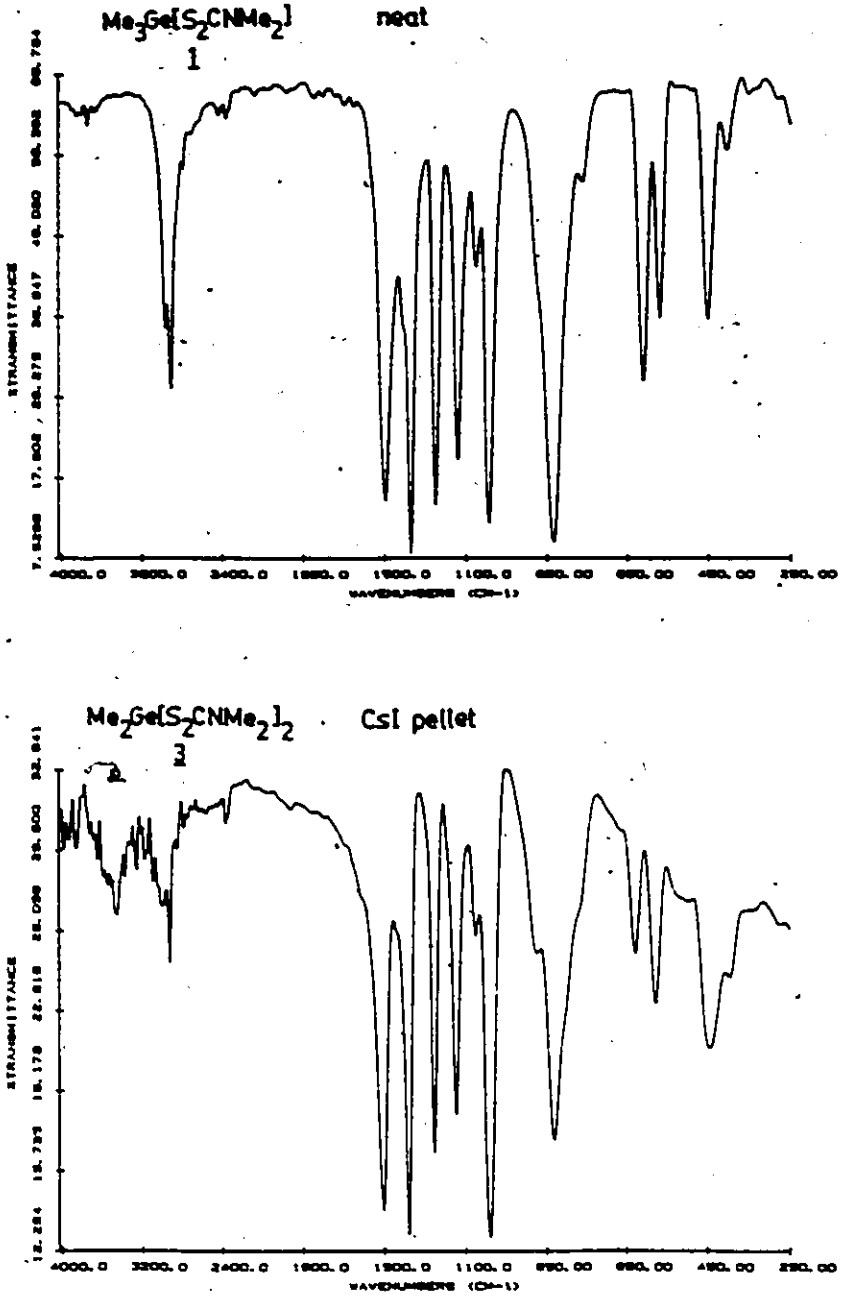


Figure 13 Infrared Spectra of Compounds 1 and 3.

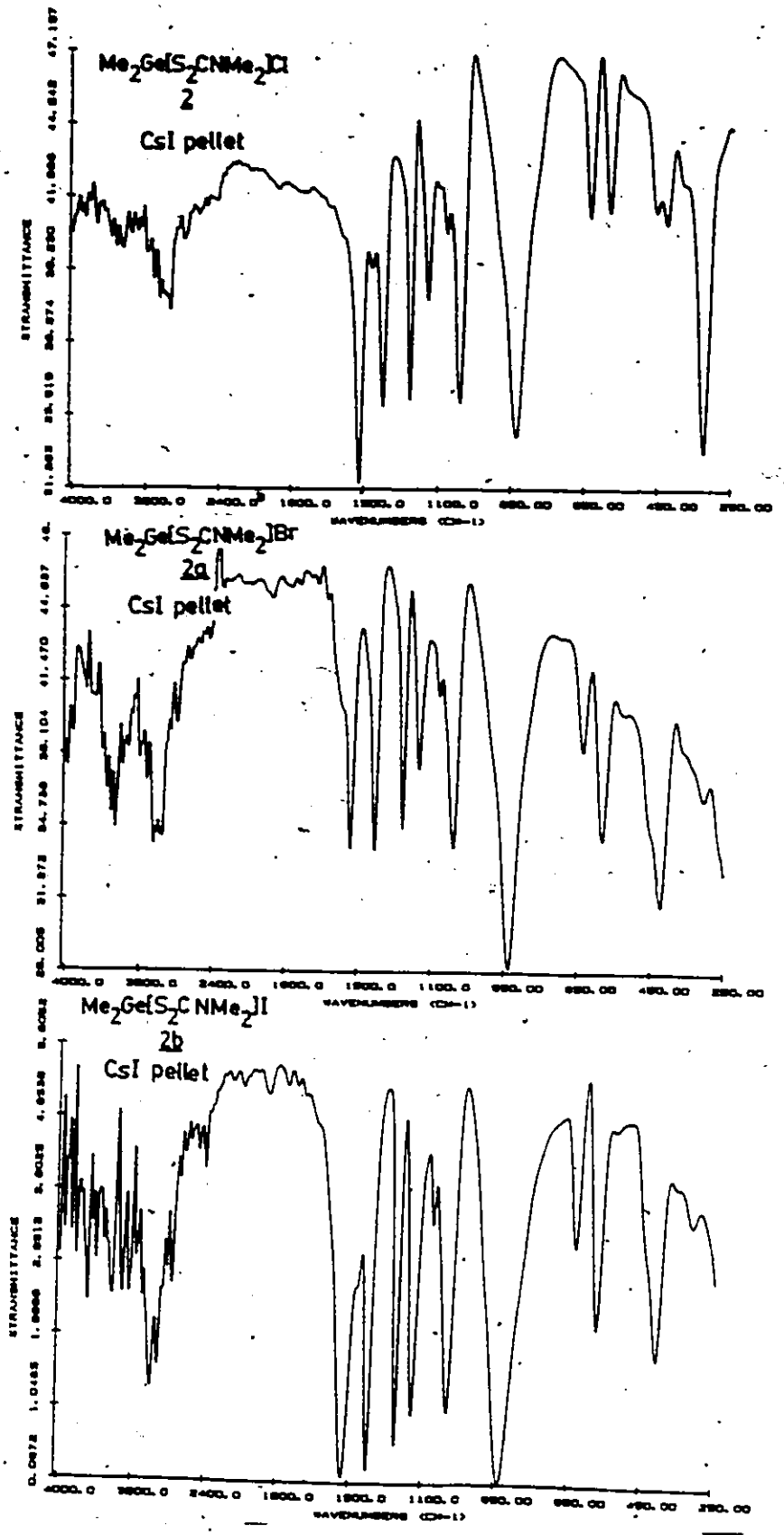


Figure 14 Infrared Spectra of Compounds 2, 2a and 2b.

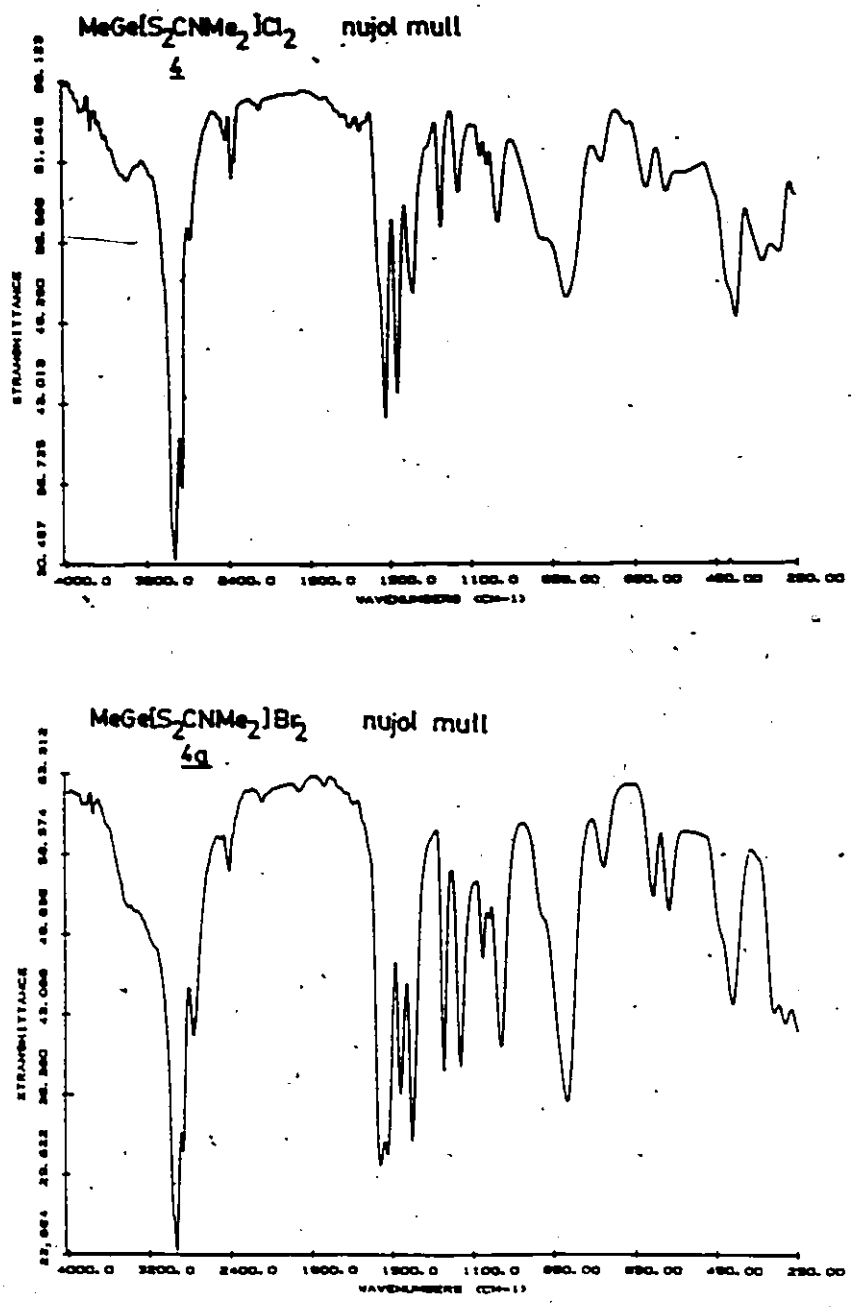


Figure 15 Infrared Spectra of Compounds 4 and 4a.

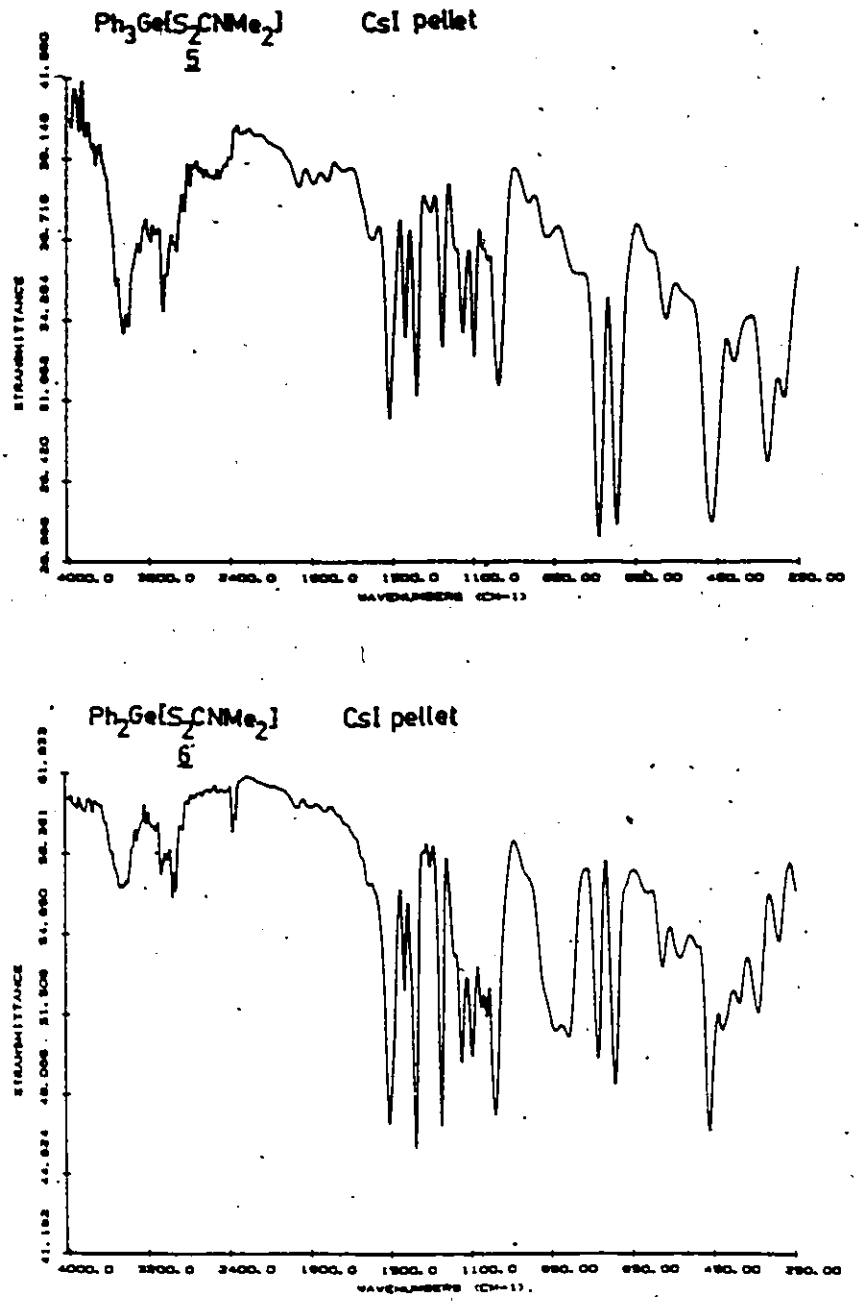
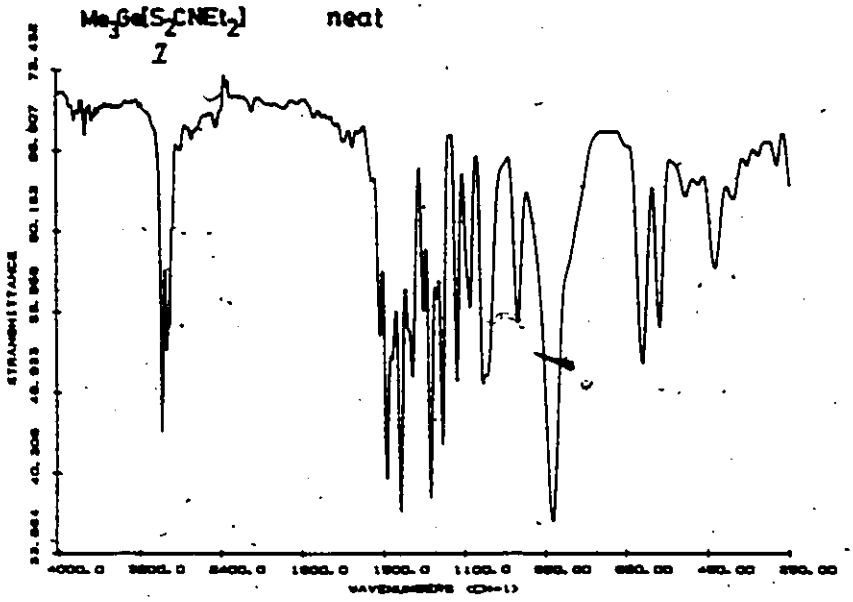


Figure 16 Infrared Spectra of Compounds 5 and 6.



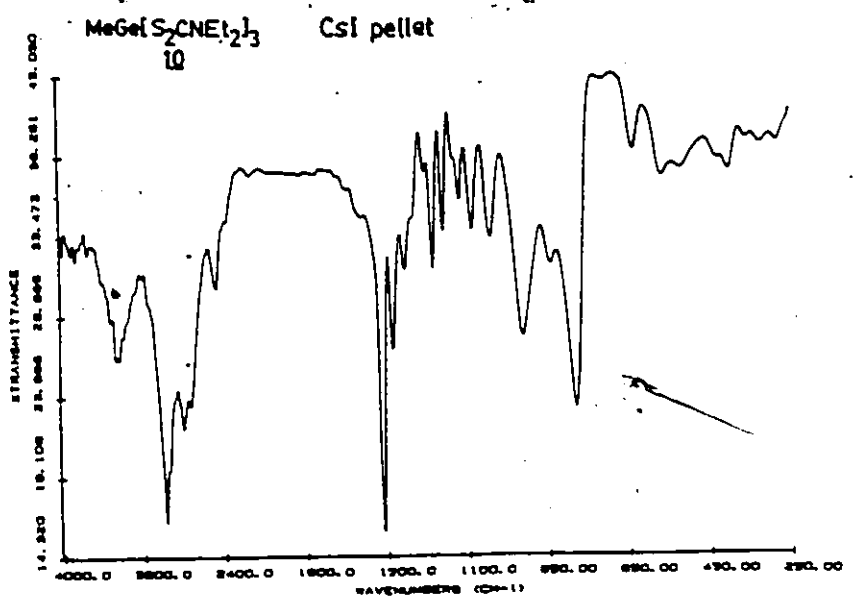


Figure 17 Infrared Spectra of Compounds 7 and 10.

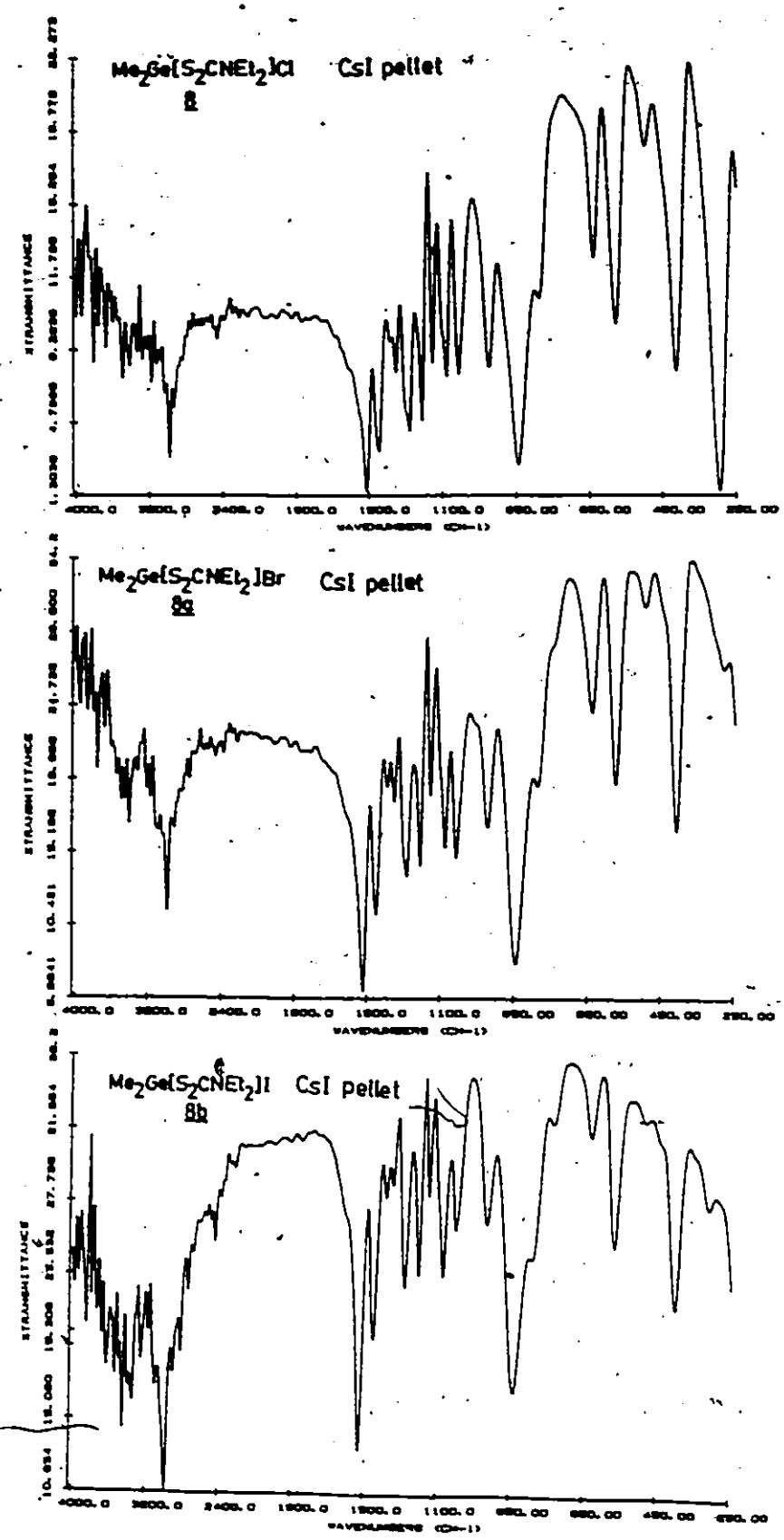
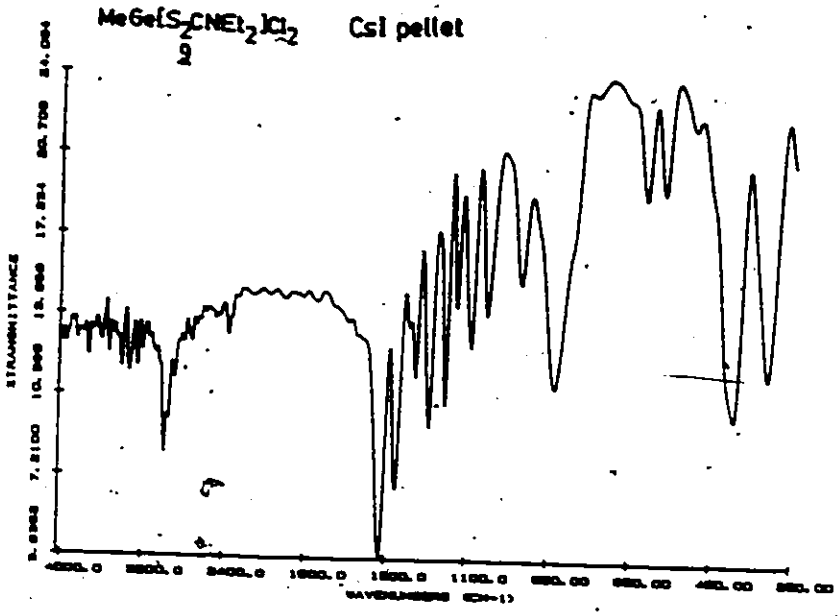


Figure 18 Infrared Spectra of Compounds 8, 8a and 8b.



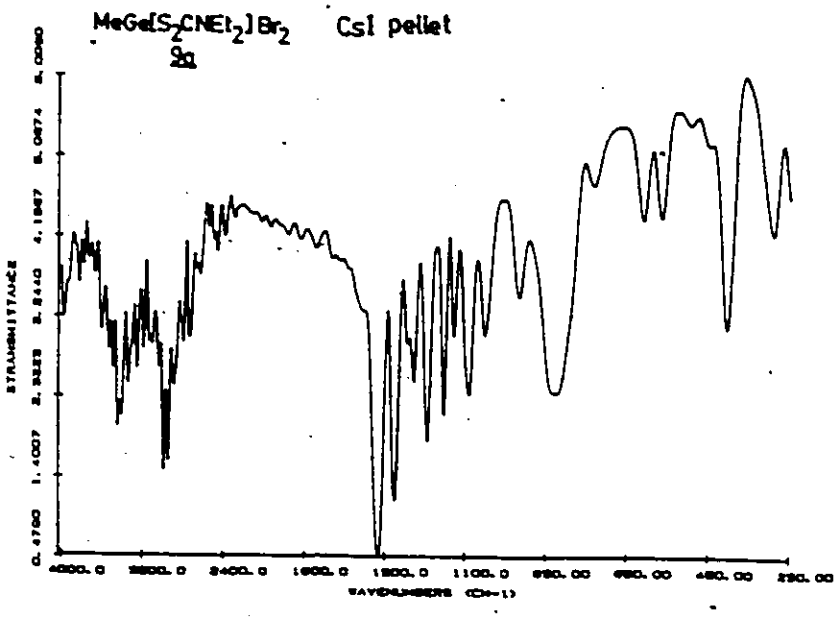


Figure 19. Infrared Spectra of Compounds 9 and 9a.

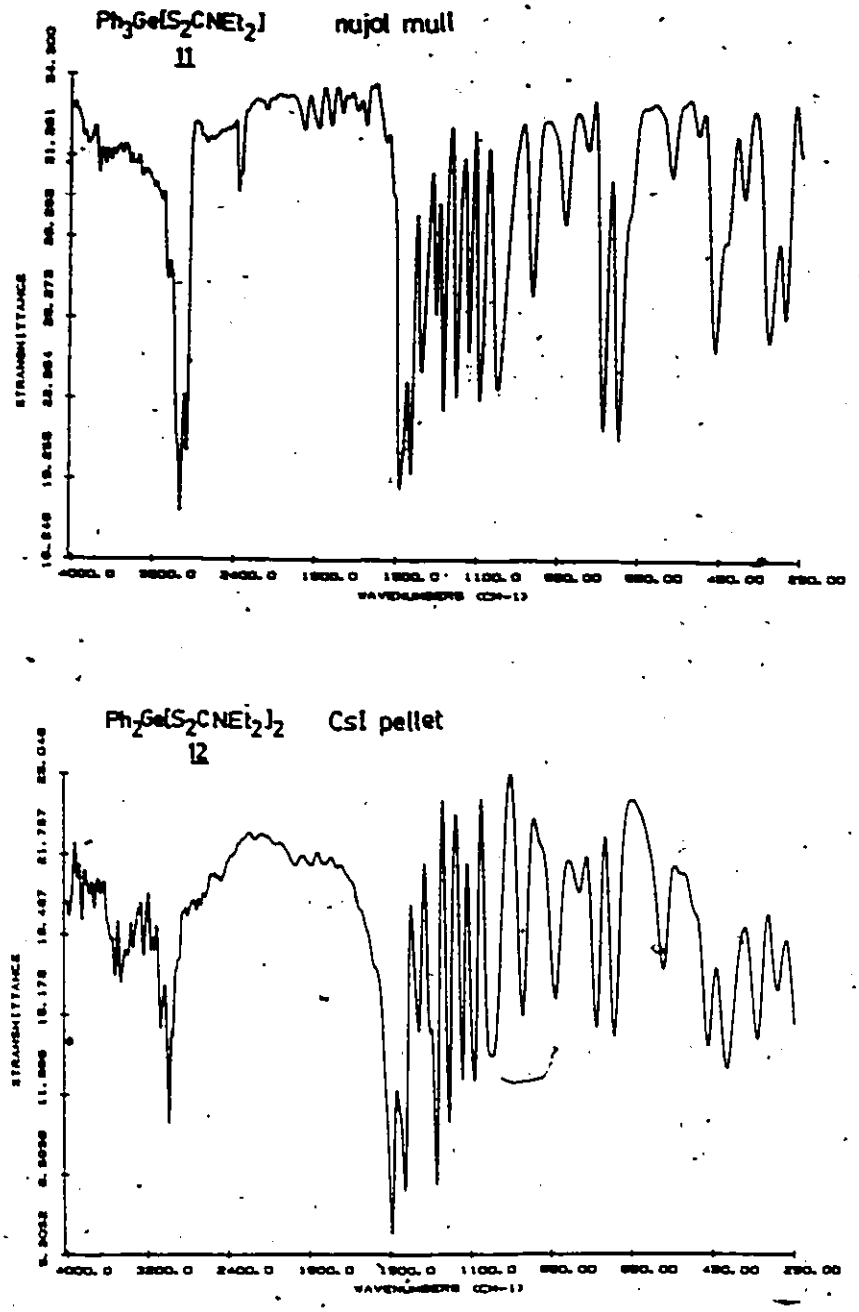


Figure 20. Infrared Spectra of Compounds 11 and 12.

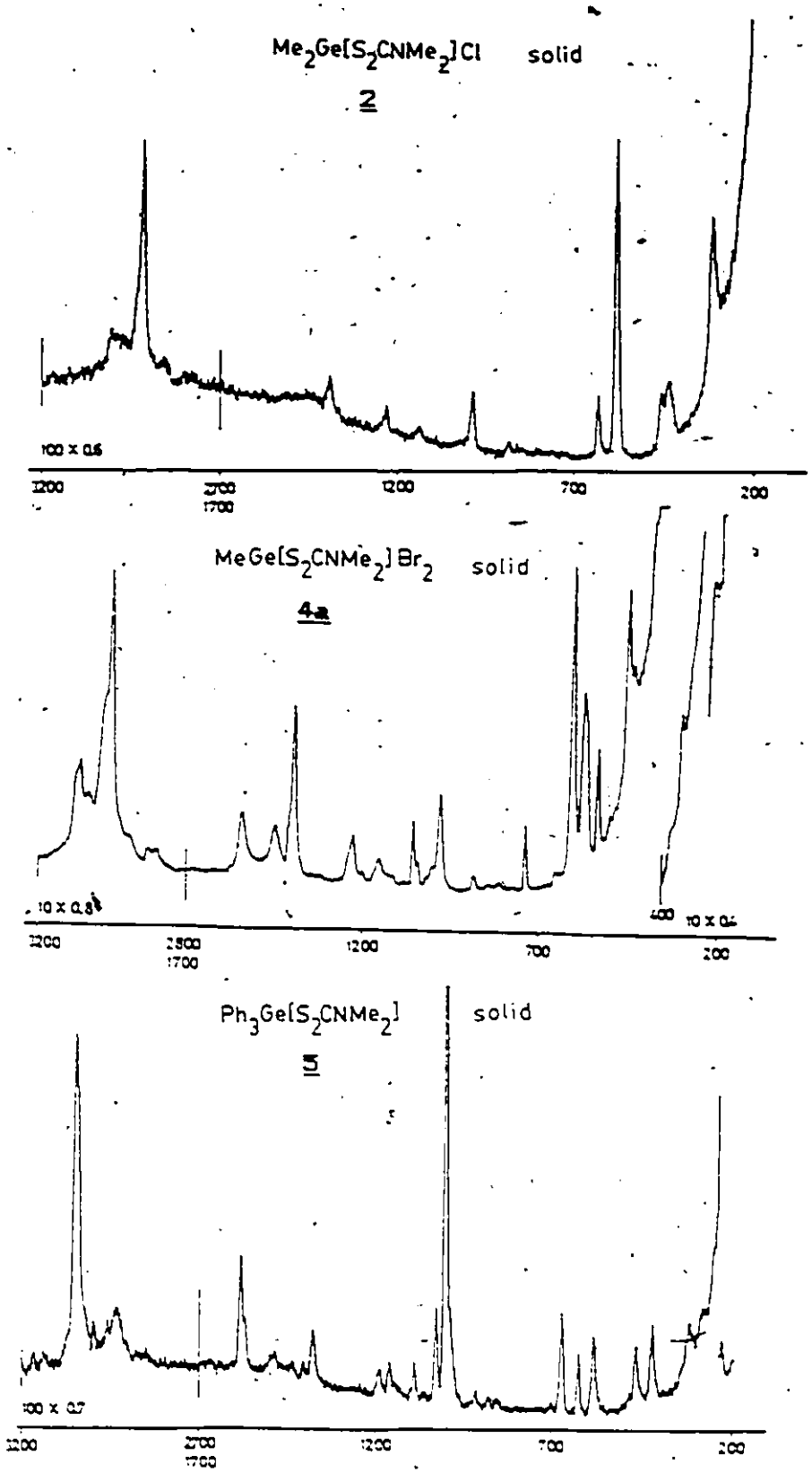


Figure 21 Raman Spectra of Compounds 2, 4a and 5.

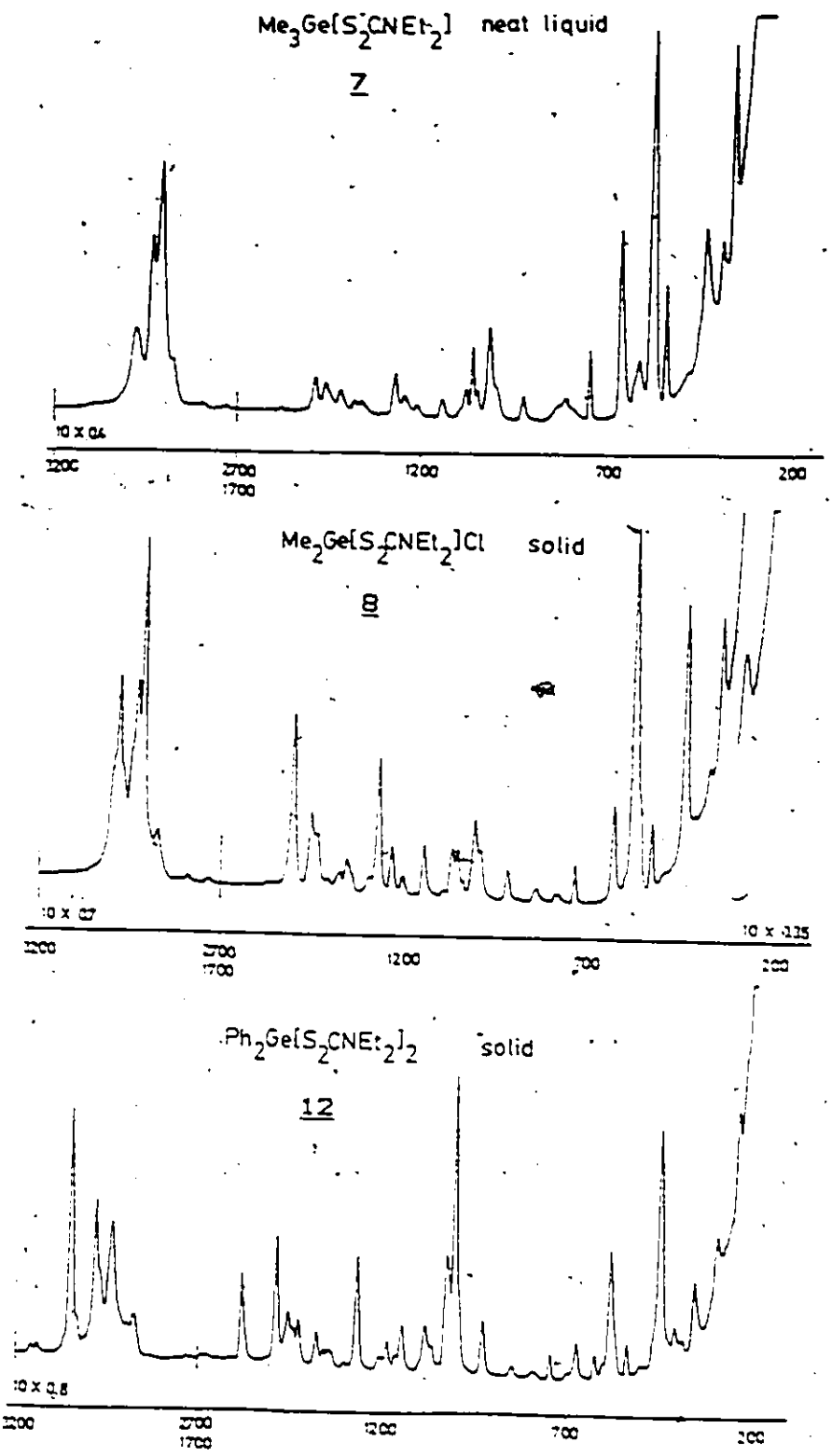


Figure 22 Raman Spectra of Compounds 7, 8 and 12.

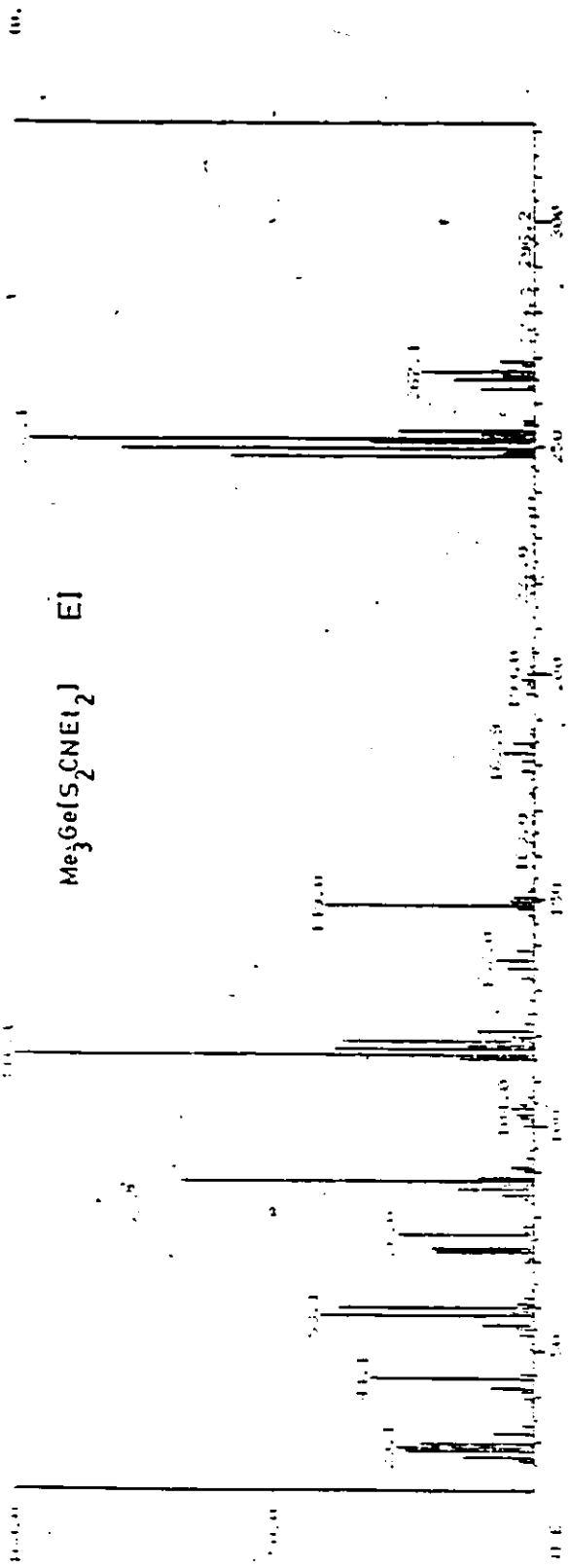
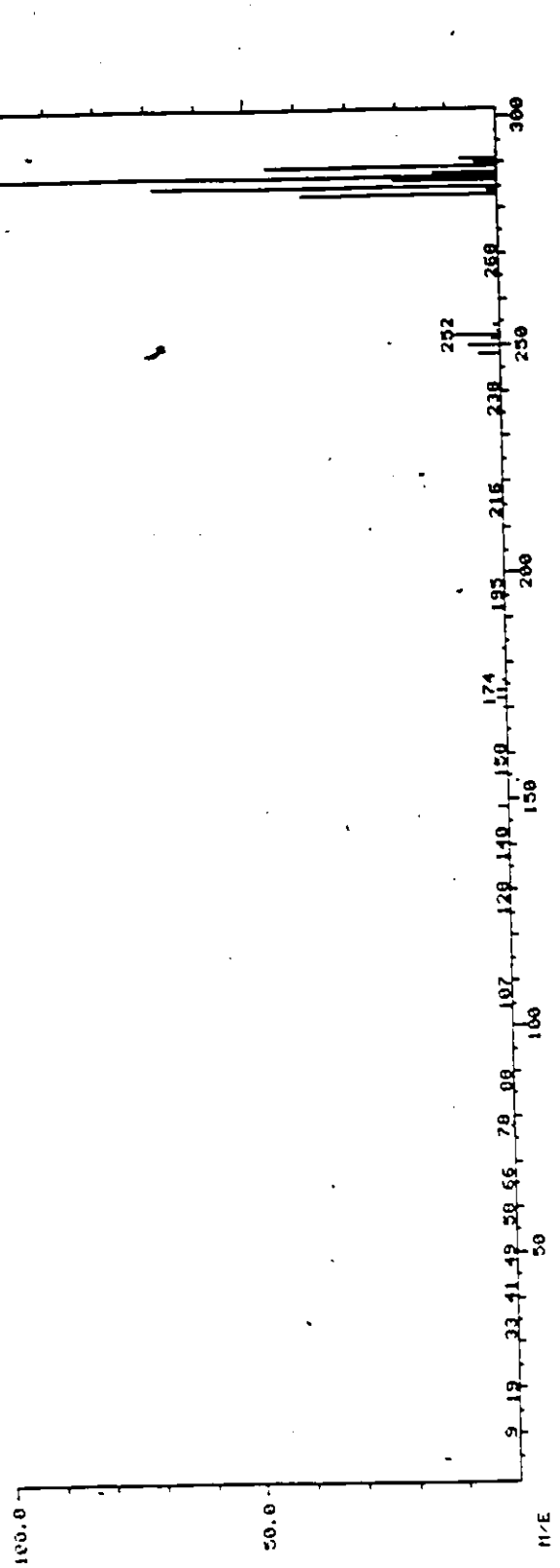


Figure 23 Electron Impact Mass Spectrum of Compound 7.

Figure 24 Field Ionization Mass Spectrum of Compound 8.



CHAPTER VI

THE PREPARATION OF ORGANOGERMANIUM DERIVATIVES OF DITHIOIPHOSPHATES

The most common route to the preparation of the dithiophosphate compounds is the reaction between excess alcohol or phenol and phosphorus(V)sulfide and subsequent quenching of the system by metal oxides, chlorides, acetates or carbonates.[96]

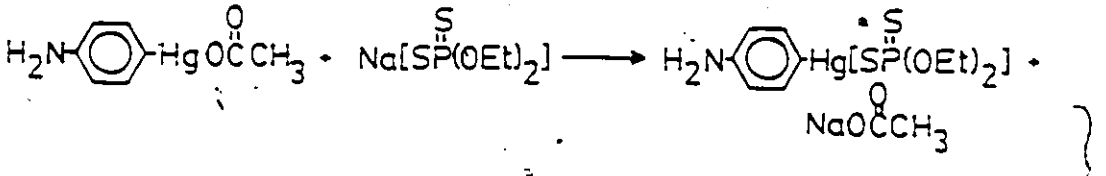
$$P_2S_5 + 4(CH_3)_2CHOH \longrightarrow 2HSP(=S)(OC_3H_7\text{-}i)_2 + H_2S\uparrow$$

$$ZnO + 2HSP(=S)(OC_3H_7\text{-}i)_2 \longrightarrow Zn[SP(=S)(OC_3H_7\text{-}i)_2]_2 + H_2O$$

The dithiophosphoric acids, which are relatively stable and separable by vacuum distillation have also been used as in[39,40]

$$(C_6H_5)_3SnOH + HSP(=S)(OC_2H_5)_2 \xrightarrow{\text{BENZENE}} (C_6H_5)_3Sn[SP(=S)(OC_2H_5)_2] + H_2O$$

Another widely utilized technique is the use of alkali metal salts.[97,98]



Typical of such reactions are the removal of water by azeotropic distillation or of alkali metal halides by precipitation, thus enhancing product formation. The following, where an alkane is produced, is an interesting variation.[99]

$$(C_2H_5)_4Sn + HSP(=S)(OC_2H_5)_2 \longrightarrow (C_2H_5)_3Sn[SP(=S)(OC_2H_5)_2] + C_2H_6\uparrow$$

Despite the knowledge that a change in the alkoxy group often results in new chemical properties, syntheses involving mixed alkoxy groups have virtually been ignored.

The organogermanium dithiophosphate esters in this work were prepared by nucleophilic replacement of one or more halogens on germanes by *O,O'*-dimethyldithiophosphate or *O,O'*-diethyldithiophosphate anions. The reactions for the preparation of *O,O'*-dimethyldithiophosphate derivatives are illustrated in Scheme 3.

SCHEME 3

a. $Me_3GeBr + NH_4[S_2P(OMe)_2] \longrightarrow Me_3Ge[S_2P(OMe)_2] + NH_4Br$ (13)

b. $Me_2GeCl_2 + 2\ NH_4[S_2P(OMe)_2] \longrightarrow Me_2Ge[S_2P(OMe)_2]_2 + 2\ NH_4Cl$ (14)

c. $MeGeCl_3 + 3\ NH_4[S_2P(OMe)_2] \longrightarrow MeGe[S_2P(OMe)_2]_3 + 3\ NH_4Cl$ (15)

d. $GeCl_4 + 2\ NH_4[S_2P(OMe)_2] \longrightarrow Cl_2Ge[S_2P(OMe)_2]_2 + 2\ NH_4Cl$ (16)

$GeBr_4 + 2\ NH_4[S_2P(OMe)_2] \longrightarrow Br_2Ge[S_2P(OMe)_2]_2 + 2\ NH_4Br$ (16a)

$GeI_4 + 2\ NH_4[S_2P(OMe)_2] \longrightarrow I_2Ge[S_2P(OMe)_2]_2 + 2\ NH_4I$ (16b)

e. $Ph_3GeCl + NH_4[S_2P(OMe)_2] \longrightarrow Ph_3Ge[S_2P(OMe)_2] + NH_4Cl$ (17)

f. $Ph_2GeCl_2 + 2\ NH_4[S_2P(OMe)_2] \longrightarrow Ph_2Ge[S_2P(OMe)_2]_2 + 2\ NH_4Cl$ (18)

g. $PhGeCl_3 + 3\ NH_4[S_2P(OMe)_2] \longrightarrow PhGe[S_2P(OMe)_2]_3 + 3\ NH_4Cl$ (19)

Preparation of trimethyl(*O,O'*-dimethyldithiophosphato)germane (13), $(CH_3)_3Ge[SP(S)(OCH_3)_2]$.

The germane, $(CH_3)_3GeBr$ (2 mmol) and the solvent, C_6H_6 (2.5 mL) were distilled onto the dry salt, $(CH_3O)_2PS(S)NH_4$ (0.412 g, 2.38 mmol). The reaction mixture was stirred for 10 h with occasional cooling to ca. −10°C. The contents were filtered, and the filtrate was allowed to evaporate on the vacuum line. The residue was distilled under vacuum (84°C, 0.20 mm Hg) to give a clear liquid. Yield 57%, n 1.5343. Anal. Calcd for $C_5H_{15}S_2PO_2Ge$: C, 21.85; H, 5.50; P, 11.27. Found: C, 22.20; H, 5.97; P, 11.68.

Preparation of dimethylbis(*O,O'*-dimethyldithiophosphato)germane (14), $(CH_3)_2Ge[SP(S)(OCH_3)_2]_2$.

The germane, $(CH_3)_2GeCl_2$ (1 mmol) and C_6H_6 (3 mL) were condensed onto previously dried $(CH_3O)_2PS(S)NH_4$ (0.503 g, 2.91 mmol). The vessel was warmed up to ambient temperature and the contents were thoroughly mixed and then maintained at ca. 10°C for 12 h. The solids in the reaction mixture were separated by filtration and the solvent was removed by evaporation. The liquid thus obtained froze at ca. 0°C and was washed with cold *n*-hexane and dried. Yield 76%, n 1.5842. Anal. Calcd for $C_6H_{18}S_4P_2O_4Ge$: C, 17.28; H, 4.35; P, 14.86. Found: C, 17.98; H, 4.79; P, 15.54.

Preparation of methyltris(*O,O'*-dimethyldithiophosphato)germane (15), $CH_3Ge[SP(S)(OCH_3)_2]_3$.

The germane, CH_3GeCl_3 (1 mmol) and the solvent, C_6H_6 (2 mL) were distilled onto dry $(CH_3O)_2PS(S)NH_4$ (0.550 g, 3.18 mmol) at −196°C. The contents were gradually warmed up to ca. 10°C and stirred vigorously for 6 h. The solid NH_4Cl was filtered off and the filtrate was slowly evaporated to give a clear oily liquid. Yield 80%, η 1.5979. Anal. Calcd for $C_7H_{21}S_6P_3O_6Ge$: C, 15.04; H, 3.79; P, 16.62. Found: C, 15.16; H, 4.00; P, 16.42.

Preparation of dichlorobis(*O,O'*-dimethyldithiophosphato)germane (16), $Cl_2Ge[SP(S)(OCH_3)_2]_2$.

The germane, $GeCl_4$ (2 mmol) and C_6H_6 (3 mL) were added to dry $(CH_3O)_2PS(S)NH_4$ (0.712 g, 4.12 mmol), at liquid nitrogen temperature. The reaction mixture was warmed up to ambient temperature and stirred moderately for 5 h with occasional cooling to 0°C. The solids in the reaction mixture were filtered off, and the filtrate on evaporation gave a clear liquid. Yield 60%, η 1.5744. Anal. Calcd for $C_4H_{12}S_4P_2O_4GeCl_2$: C, 10.49; H, 2.64; Cl, 15.49. Found: C, 10.33; H, 2.81; Cl, 15.38.

Preparation of dibromobis(*O,O'*-dimethyldithiophosphato)germane (16a), $Br_2Ge[SP(S)(OCH_3)_2]_2$.

Frozen $GeBr_4$ (0.473 g, 1.20 mmol) was added to dry $(CH_3O)_2PS(S)NH_4$ (0.698 g, 4.04 mmol) under nitrogen atmosphere and the vessel was immediately evacuated. The solvent, C_6H_6

(3 mL) was distilled in and the reaction mixture was stirred for 5 h at ca. 10°C. The cream colored mixture was filtered and the solvent was pumped off on the vacuum line to obtain a clear yellowish liquid. The liquid was washed with ligroin and dried under vacuum. Yield 65%, n 1.6302. Anal. Calcd for $C_4H_{12}S_4P_2O_4GeBr_2$: C, 8.79; H, 2.21. Found: C, 9.64 ; H, 2.27.

In a separate experiment with a prolonged reaction time a few colorless crystals (mp 152°C) were obtained, which are probably the tris derivative, $BrGe[SP(S)(OCH_3)_2]_3$.

Preparation of diiodobis(*O,O'*-dimethyldithiophosphato)germane (16 b), $I_2Ge[SP(S)(OCH_3)_2]_2$.

The salt, $(CH_3O)_2PS(S)NH_4$ (0.568 g, 3.28 mmol) was mixed with powdered GeI_4 (0.596 g, 1.03 mmol) and the reaction vessel was evacuated. The solvent, C_6H_6 (3 mL) was distilled in and upon warming a hay colored mixture resulted which was stirred moderately at ca. 10°C. The solid NH_4I and the unreacted salt, $(CH_3O)_2PS(S)NH_4$, were separated by filtration and the solvent was pumped off. The clear yellow liquid thus obtained was washed with ligroin and dried under vacuum. Yield 75%, n 1.6575. Anal. Calcd for $C_4H_{12}S_4P_2O_4GeI_2$: C, 7.50; H, 1.89. Found: C, 10.59 ; H, 2.57.

Under the same conditions, with the exception of a longer reaction time, a few yellow crystals (mp 44°C) were obtained, which are probably $IGe[SP(S)(OCH_3)_2]_3$.

Preparation of triphenyl(*O,O'*-dimethyldithiophosphato)germane (17), $(C_6H_5)_3Ge[SP(S)(OCH_3)_2]$.

The solvent, C_6H_6 (3 mL) was distilled under vacuum onto a mixture of $(C_6H_5)_3GeCl$ (0.345 g, 1.02 mmol) and dry $(CH_3O)_2PS(S)NH_4$ (0.271 g, 1.57 mmol). The mixture was slowly warmed up to ambient temperature and stirred moderately for 3 h. The reaction vessel was occasionally cooled to 0°C to slow down the reaction and left undisturbed at 0°C for 12 h. Solid NH_4Cl was filtered off and the filtrate was slowly evaporated under vacuum. The colorless solid product thus obtained was recrystallized from CS_2 in the refrigerator to give transparent crystals. Yield 70%, mp 96°C. Anal. Calcd for $C_{20}H_{21}S_2PO_2Ge$: C, 52.10; H, 5.49. Found: C, 52.41; H, 4.70.

Preparation of diphenylbis(*O,O'*-dimethyldithiophosphato)germane (18), $(C_6H_5)_2Ge[SP(S)(OCH_3)_2]_2$.

A solution of $(C_6H_5)_2GeCl_2$ (0.308 g, 1.03 mmol) and C_6H_6 (3.5 mL) was added to the dry salt, $(CH_3O)_2PS(S)NH_4$ (0.450 g, 2.60 mmol) under a nitrogen atmosphere. The mixture was quickly frozen in liquid nitrogen and the reaction vessel was evacuated on a vacuum line. The reaction mixture was gradually warmed to ambient temperature and stirred continuously for 12 h with occasional cooling to 0°C. The vessel was cooled to 0°C and the solid NH_4Cl was separated by filteration. The solvent was slowly evaporated and a colorless powder formed. The product was dissolved in CS_2 and recrystallized in the refrigerator.

Yield 78%, mp 92°C. Anal. Calcd for $C_{14}H_{22}S_6P_2O_6Ge$: C, 35.91; H, 4.10. Found: C, 35.24; H, 3.92.

Preparation of phenyltris(*O,O'*-dimethyldithiophosphato)germane (19), $C_6H_5Ge[SP(S)(OCH_3)_2]_3$.

A solution of $C_6H_5GeCl_3$ (0.248 g, 0.97 mmol) in C_6H_6 (2.5 mL) was added under nitrogen to the previously dried salt, $(CH_3O)_2PS(S)NH_4$ (0.571 g, 3.30 mmol). The contents were immediately frozen (−196°C) and the reaction vessel was immediately evacuated. The reaction mixture was warmed up to ambient temperature and stirred with occasional cooling for 6 h prior to filtration. The solvent was immediately evaporated off under vacuum. The quasi-solid white residue obtained was recrystallized from CS_2 in the refrigerator. Yield 63%, mp 55°C. Anal. Calcd for $C_{12}H_{23}S_6P_3O_6Ge$: C, 23.20; H, 3.73. Found: C, 23.20; H, 3.71.

Essentially similar procedures were followed to prepare the *O,O'*-diethyldithiophosphato derivatives. The germanes were reacted with the ammonium salt of *O,O'*-diethyldithiophosphoric acid according to Scheme 4.

SCHEME 4

a. $Me_3GeBr + NH_4[S_2P(OEt)_2] \longrightarrow Me_3Ge[S_2P(OEt)_2] + NH_4Br$ (20)

b. $Me_2GeCl_2 + 2\ NH_4[S_2P(OEt)_2] \longrightarrow Me_2Ge[S_2P(OEt)_2]_2 + 2\ NH_4Cl$ (21)

c. $MeGeCl_3 + 3\ NH_4[S_2P(OEt)_2] \longrightarrow MeGe[S_2P(OEt)_2]_3 + 3\ NH_4Cl$ (22)

d. $Ph_3GeCl + NH_4[S_2P(OEt)_2] \longrightarrow Ph_3Ge[S_2P(OEt)_2] + NH_4Cl$ (23)

e. $Ph_2GeCl_2 + 2\ NH_4[S_2P(OEt)_2] \longrightarrow Ph_2Ge[S_2P(OEt)_2]_2 + 2\ NH_4Cl$ (24)

f. $PhGeCl_3 + 3\ NH_4[S_2P(OEt)_2] \longrightarrow PhGe[S_2P(OEt)_2]_3 + 3\ NH_4Cl$ (25)

Preparation of trimethyl(*O,O'*-diethyldithiophosphato)germane (20), $(CH_3)_3Ge[SP(S)(OC_2H_5)_2]$.

The germane, $(CH_3)_3GeBr$ (2 mmol) and the solvent, C_6H_6 (2 mL) were condensed into previously dried $(C_2H_5O)_2PS(S)NH_4$ (0.470 g, 2.34 mmol) in sequence. The reaction vessel was warmed up to ca. 10°C and the mixture was stirred moderately for 5 h. The solid NH_4Br was filtered off and the filtrate was slowly evaporated under vacuum to obtain a clear liquid. Yield 80%, n 1.5196. Anal. Calcd for $C_7H_{17}S_2PO_2Ge$: C, 27.76; H, 6.32; P, 10.23. Found: C, 27.62; H, 5.94; P, 10.47.

Preparation of dimethylbis(*O,O'*-diethyldithiophosphato)germane (21), $(CH_3)_2Ge[SP(S)(OC_2H_5)_2]_2$.

The germane, $(CH_3)_2GeCl_2$ (1.3 mmol) and C_6H_6 (3 mL) were distilled onto the dry salt, $(C_2H_5O)_2PS(S)NH_4$ (0.562 g, 2.79 mmol). The contents were warmed up and stirred vigorously with occasional cooling (ca. −10°C) for 4 h. The solids in the reaction mixture were separated by filtration and the volatile materials were pumped off from the filtrate to give a clear liquid. Yield 82%, n 1.5439. Anal. Calcd for $C_{10}H_{24}S_4P_2O_4Ge$: C, 25.39; H, 5.54; P, 13.09. Found: C, 24.10; H, 4.99; P, 12.71.

Preparation of methyltris(*O,O'*-diethyldithiophosphato)germane (22), $CH_3Ge[SP(S)(OC_2H_5)_2]_3$.

The germane, CH_3GeCl_3 (1 mmol) and C_6H_6 (3 mL) were distilled on in sequence onto dry $(C_2H_5O)_2PS(S)NH_4$ (0.734 g, 3.65 mmol) held at −196°C. The reaction vessel was warmed up to ca. 15°C and stirred for 5 h. The solid NH_4Cl was removed by filtration, and the filtrate on slow evaporation gave a clear liquid. Yield 52%, n 1.5753. Anal. Calcd for $C_{13}H_{33}S_6P_3O_6Ge$: C, 24.27; H, 5.17. Found: C, 23.93; H, 4.98.

Preparation of triphenyl(*O,O'*-diethyldithiophosphato)germane (23), $(C_6H_5)_3Ge[SP(S)(OC_2H_5)_2]$.

The dry salt, $(C_2H_5O)PS(S)NH_4$ (0.249g, 1.24 mmol) was mixed with crushed $(C_6H_5)_3GeCl$ (0.350 g, 1.03 mmol) and the reaction

vessel was evacuated prior to distilling in the solvent, C_6H_6 (2.5 mL). The reaction mixture was allowed to warm up and was stirred vigorously at ambient temperature for 4 h. The solids in the mixture were separated by filtration and the solvent was pumped off under vacuum. The white residue thus obtained was dissolved in fresh CS_2 and recrystallized in the refrigerator and washed with ligroin. Yield 85%, mp 113°C. Anal. Calcd for $C_{22}H_{25}S_2PO_2Ge$: C, 54.02; H, 5.15; P, 6.33. Found: C, 53.94; H, 5.04; P, 6.06.

Preparation of diphenylbis(*O,O'*-diethyldithiophosphato)germane (24), $(C_6H_5)_2Ge[SP(S)(OC_2H_5)_2]_2$.

A solution of $(C_6H_5)_2GeCl_2$ (0.311 g, 1.05 mmol) and C_6H_6 (2 mL) was added to the dry salt, $(C_2H_5O)_2PS(S)NH_4$ (0.475 g, 2.36 mmol) under nitrogen atmosphere. The reaction mixture was immediately frozen by liquid nitrogen and the reaction vessel evacuated. The contents were warmed up to ambient temperature and stirred for 10 h. Solid NH_4Cl was filtered off and the filtrate was slowly evaporated under vacuum. The clear liquid thus obtained was washed with ligroin and dried. Yield 80%, n 1.6080. Anal. Calcd for $C_{20}H_{30}S_4P_2O_4Ge$: C, 40.22; H, 5.06; P, 10.37. Found: C, 39.84; H, 4.81; P, 9.78.

Preparation of phenyltris(*O,O'*-diethyldithiophosphato)germane (25), $C_6H_5Ge[SP(S)(OC_2H_5)_2]_3$.

A solution of $C_6H_5GeCl_3$ (0.275 g, 1.07 mmol) and C_6H_6

(3.5 mL) was added to the dry salt, $(C_2H_5O)_2PS(S)NH_4$ (0.621 g, 3.08 mmol) under nitrogen. The contents were frozen by liquid nitrogen and after evacuation, the vessel was warmed up to ca. 15°C and stirred for 10 h. NH_4Cl was removed by filtration and the filtrate was gradually evaporated under vacuum to give a clear liquid which was washed with ligroin and dried on the vacuum line. Yield 72%, n 1.5960. Anal. Calcd for $C_{18}H_{35}S_4P_2O_4Ge$: C, 30.65; H, 5.00. Found: C, 30.31; H, 4.49.

The compounds (13 - 25) illustrated in Schemes 3 and 4 are air stable, moderately hygroscopic, highly soluble in common organic solvents and repulsive in odour. Only one of the compounds, trimethyl(*O,O'*-dimethyldithiophosphato)germane (13) could be distilled without decomposition and for all of the others, decomposition preceded distillation. Thus, for example when an attempt was made to distil dimethylbis(*O,O'*-dimethyldithiophosphato)germane (14) as soon as two drops of the compound (44°C, 0.18 mm Hg) were collected the pressure fluctuated drastically, indicating decomposition was occurring. The crystals obtained from both *O,O'*-dimethyldithiophosphoric acid and *O,O'*-diethyldithiophosphoric acid salts were soft and needed special care in handling. In the reactions of methyl and phenyl germanes with the dithiophosphoric acid salts no evidence of the formation of partially substituted intermediate compounds was noted by ^1H nmr spectroscopy.

CHAPTER VII

THE CHARACTERIZATION OF ORGANOGERMANIUM DITHIOPHOSPHATES

The inorganic and organometallic dithiophosphate complexes have been extensively studied by spectroscopic methods primarily for the purpose of identification. Despite the amount of vibrational data available, no normal coordinate analysis has been reported. Thus, assignments of a number of bands remain controversial.[100] For example, the $\nu(O-CH_3)$ stretch has been assigned to bands in both the 1170 - 1095 cm^{-1} region as well as the 1015 - 965 cm^{-1} region, and the $\nu(PO_2)$ band has been placed in the 1015 - 965 cm^{-1} and 875 - 730 cm^{-1} regions.[39] ^1H and ^{31}P nmr spectra of dithiophosphate complexes have also been reported.[101-103] However, there is a conspicuous absence of any attempt to relate the bonding mode of the dithiophosphate group to the spectroscopic results.

The (*O,O'*-dialkyldithiophosphato)germanes (13 - 25) illustrated in Schemes 3 and 4 were characterized by ^1H nmr, $^{13}C\{^1H\}$ nmr, ^{31}P nmr, vibrational spectroscopy and mass spectrometry. ^1H nmr spectra served as the initial means of identification as well as an indication of the purity of the compounds. In the ^{13}C nmr spectra the $^2J_{POC}$ coupling (OCH_3 and OCH_2 peaks) was often unresolved despite large number of scans. ^{31}P nmr spectra were recorded with and without ^1H coupling. Ir spectra were recorded in CCl_4 or CS_2 and in nujol. No significant shift in peak positions was noted with the various sampling methods. Mass spectra were taken mainly in the FI (field ionization) mode, since the EI (electron impact) spectra were dominated by ligand peaks.

VII.1 ^{1}H, $^{13}C\{^{1}H\}$ and ^{31}P NMR Spectra

The ^{1}H nmr spectra of the compounds (13 to 25) are shown in Figures 25 to 29 and the data are summarized in Tables 21 and 22. The ^{13}C nmr spectra of some compounds are shown in Figures 30 and 31, and the chemical shifts are listed in Tables 23 and 24. The ^{31}P nmr spectra of some compounds are shown in Figures 32 to 34 and the chemical shifts are listed in Table 25. The ^{1}H nmr spectra of the *O,O'*-dimethyldithiophosphate derivatives show OCH_3 peaks as doublets due to $^{3}J_{POCH}$ coupling (ca. 15 Hz), as observed in analogous tin compounds.[39,40] For methylgermane and halogermane derivatives the OCH_3 shifts range between 3.59 and 3.80 ppm, while for the phenylgermyl dimethyldithiophosphates the OCH_3 resonance is observed at a slightly higher field, centered around 3.3 ppm.

For *O,O'*-diethyldithiophosphates, the OCH_2 signal appears as a quartet or multiplet due to an overlap of quartets, with chemical shifts ranging between 3.67 and 4.07 ppm. The methyl proton signals of the ethoxy group vary in the range of 0.89 to 1.33 ppm and appear as distorted triplets. The $Ge-C_6H_5$ signals for all the dithiophosphates appear as two sets of multiplets, with chemical shifts centered around 7.5 ppm. The $Ge-CH_3$ chemical shifts of the *O,O'*-dimethyldithiophosphates are almost identical to those of corresponding *O,O'*-diethyldithiophosphate derivatives. The chemical shift of trimethyl (0.67, 0.65 ppm), dimethyl (1.29, 1.21 ppm) and methylgermane (1.76, 1.73 ppm) dithiophosphates can be compared to the chloromethylgermane

series $(CH_3)_3GeCl$ (0.78 ppm), $(CH_3)_2GeCl_2$ (1.14 ppm) and CH_3GeCl_3 (1.70 ppm).[81] Thus, the effect of the dithiophosphate group can be best described as that of a halogen atom with an electronegativity close to that of chlorine.

In the $^{13}C\{^1H\}$ nmr spectra of *O,O'*-dimethyldithiophosphates the $O\underline{C}H_3$ signal appears around 54 ppm and is often seen as a doublet due to $^2J_{POC}$ coupling.[103] For the *O,O'*-diethyldithiophosphate derivatives, the $O\underline{C}H_2$ signal appears as a doublet (J = 4.4 - 7.4 Hz) in the 63.6 to 64.6 ppm range, while the $\underline{C}H_3$ resonance of the ethoxy group appears around 15.5 ppm. The consistency of positions of the methoxy and ethoxy signals indicate that a similar bonding mode is expected in all the germanium dithiophosphates. The Ge-$\underline{C}H_3$ chemical shifts of trimethyl (3.2, 3.6 ppm), dimethyl (9.2, 9.3 ppm) and methyl (13.7, 15.9 ppm) germanium dithiophosphates are similar to those of the corresponding chloromethylgermanes, $(CH_3)_3GeCl$ (4.8 ppm), $(CH_3)_2GeCl_2$ (10.7 ppm) and CH_3GeCl_3 (15.9 ppm).[81] The $^{13}C\{^1H\}$ nmr spectra are consistent with the observation that dithiophosphates have a similar effect as a chlorine atom as was observed in the ^1H nmr spectra.

The $^{31}P\{^1H\}$ chemical shifts of the dithiophosphates vary in the range of 95.6 to 80.4 ppm. The values are not significantly different from the corresponding ammonium salts of dimethyldithiophosphoric acid (95.6 ppm) and diethyldithiophosphoric acid (111.0 ppm). Analogous tin and arsenic[105] compounds also have resonances in this range. These values do not change much with

different modes of bonding, probably due to π-electron flow into vacant d-orbitals of phosphorus so that the electron density on the phosphorus atom does not vary significantly. The $^3J_{POCH}$ coupling constants can be more accurately measured from ^{31}P nmr spectra than ^1H nmr spectra due to the absence of J_{CH} coupling.

Surprisingly, compounds containing more than one ^{31}P nucleus display either a single peak or exactly the same number of peaks as the number of phosphorus atoms present. Thus, dimethyl(*O,O'*-dimethyldithiophosphato)germane (14) and diphenyl-(*O,O'*-dimethyldithiophosphato)germane (18) exhibit single sharp peaks, while dimethyl(*O,O'*-diethyldithiophosphato)- germane (21) and phenyltris(*O,O'*-dimethyldithiophosphato)- germane (19) display two and three peaks respectively. The dissymmetry of phosphorus atoms might be due to the result of disorder of the alkoxy groups causing a difference in electron densities on the phosphorus atoms.

VII. 2 Infrared and Raman Spectra

A number of infrared and Raman spectra of (*O,O'*-dialkyl-dithiophosphato)germanes are illustrated in Figures 35 to 41 and their frequencies are displayed in Tables 26 to 30. The compounds show the basic dithiophosphate bands, $\nu(O-CH_3)$ around 1000 cm^{-1}, $\nu(PO_2)$ in the 800 cm^{-1} region and a clear distinctive terminal $\nu(P=S)$ band around 650 cm^{-1}.[105] The complexity of the spectra increases with the introduction of ethoxy and phenyl groups. For the methylgermyl derivatives, the spectra may be

considered as superimpositions of the methylgermane spectrum onto that of the dithiophosphate moiety. For the dithiophosphates containing Ge–C_6H_5 groups, the spectra are dominated by bands of monosubstituted benzene rings, which are relatively insensitive to the dithiophosphate group.[82] An extensive study of $(C_6H_5)_3GeX$, $(C_6H_5)_2GeX_2$ and $C_6H_5GeX_3$ emphasized this fact and illustrated that assignments should be made to the phenylgermyl group as a whole, and no distinction on the basis of the number of phenyl groups can be made.[107–109] Thus, no specific assignments to the ν(Ge–C_2) or ν(Ge–C_3) bands are made in contrast to the assignment of ν(Ge–C) bands in the methylgermanes. Inclusion of assignments of methyl and phenyl germanes along with those for $(CH_3O)_2P(S)SCH_3$[110] makes the assignments of the vibrational bands of the organogermanium dithiophosphates essentially self-evident. The dihalobis-(*O*,*O*'-dimethyldithiophosphato)germane (16 – 16b) series, which do not contain methyl or phenyl groups on germanium, show clear ν(O–CH_3), ν(PO_2) and ν(P=S) bands. The bridging ν(P–S) stretches appear in the 525 – 490 cm^{-1} region. In fact, these bands along with the ν(P=S) band may be indicative of the bonding mode of dithiophosphates. In the ammonium salt of *O*,*O*'-dimethyl-dithiophosphoric acid, which presumably does not contain an isolated P=S bond, these bands are not evident. However, in the free acid and the ester, $(CH_3O)_2P(S)SCH_3$, the ν(P=S) and the ν(P–S) bands are clear features. Thus, infrared data of dithiophosphates strongly suggest a monodentate mode of attachment. The

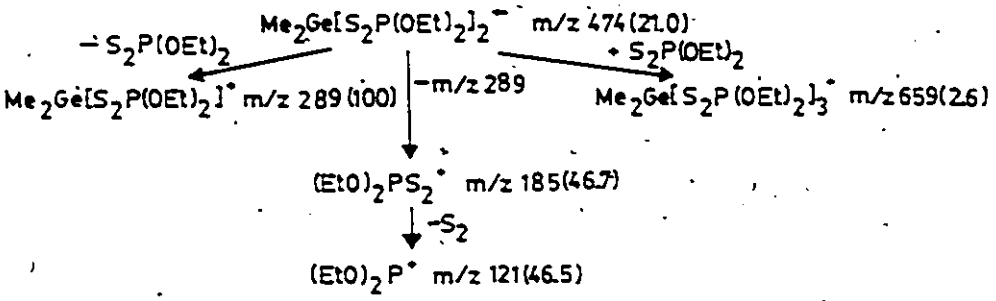
similarity of the ν(Ge–C) symmetric and asymmetric vibrations of chloromethylgermanes[84–88,92] to those of methylgermanium dithiophosphates are consistent with the assumption that the effect of dithiophosphate substitution is, in effect, equivalent to that of a chlorine atom. For example, in the ir spectrum of dimethyl(*O,O'*-dimethydithiophosphato)germane (14) the ν(Ge–C) symmetric and asymmetric stretches appear at 638 and 579 cm^{-1} and for $(CH_3)_2GeCl_2$ the corresponding bands are observed at 640 and 594 cm^{-1} respectively. In trimethyl(*O,O'*-dimethyldithiophosphato)-germane (13) these values are 609 and 568 cm^{-1} compared to 612 and 569 cm^{-1} for $(CH_3)_3GeCl$. The ν(Ge–X) stretches for the dihalo(*O,O'*-dimethyldithiophosphato)germane appear at 382, 284 and 232 cm^{-1} for chloro, bromo and iodo derivatives (16 – 16b) respectively, indicating that the pseudo-tetrahedral geometry around germanium is essentially retained.

VII.3 Mass Spectra

The mass spectral data of the dithiophosphate compounds are presented in Tables 31 to 35, and the mass spectra of two representative compounds are illustrated in Figures 42 and 43. The fragmentation pattern of the compounds are relatively simple and may be compared to halomethyl and halophenylgermanes,[92] and analogous tin dithiophosphates.[89,90]

The germanium containing clusters are readily recognizable by their distinct isotope pattern. Molecular ions are not seen for some compounds even in the FI mode. However, in the FI

spectra of trimethyl(*O,O'*-dimethyldithiophosphato)germane (13), trimethyl(*O,O'*-diethyldithiophosphato)germane (20) and triphenyl-(*O,O'*-diethyldithiophosphato)germane (23), the $M^{+\cdot}$ ions dominate the spectra. A representative fragmentation pattern is shown below.



Interestingly, association peaks corresponding to the molecular ion and the ligand are observed for compound 13, 20 and dimethylbis(*O,O'*- diethyldithiophosphato)germane (21) at m/z 433, 489 and 659 respectively. The formation of free acid peaks at m/z 158 and m/z 186 and their oligomers are evident in all compounds. The compounds display a clear preference to form clusters corresponding to $[M-L]^+$ fragments over $[M-CH_3]^+$ or $[M-C_6H_5]^+$ fragments. Thus it seems reasonable to assume that the germanium atom is linked by only one sulfur atom and the molecules possess monodentate dithiophosphate groups.

Table 21 ^1H nmr Data of *O,O'*-Dimethyldithiophosphoric Acid Derivatives of Methyl and Phenylgermanes[a]

Compound	No.	Chemical Shift δ in ppm[b] Ge-CH_3/C_6H_5	O-CH_3	$^3J_{POCH}$ (Hz)
$(CH_3)_3Ge[S_2P(OCH_3)_2]$	13	0.67(9H)	3.59(6H, d)	14.4
$(CH_3)_2Ge[S_2P(OCH_3)_2]_2$	14	1.29(6H)	3.69(12H, d)	15.0
$CH_3Ge[S_2P(OCH_3)_2]_3$	15	1.76(3H)	3.73(18H, d)	15.6
$Cl_2Ge[S_2P(OCH_3)_2]_2$	16		3.79(d)	16.2
$Br_2Ge[S_2P(OCH_3)_2]_2$	16a		3.80(d)	16.0
$I_2Ge[S_2P(OCH_3)_2]_2$	16b		3.78(d)	15.0
$(C_6H_5)_3Ge[S_2P(OCH_3)_2]$	17	7.2 - 7.6(15H)	3.27(6H, d)	15.0
$(C_6H_5)_2Ge[S_2P(OCH_3)_2]_2$	18	7.2 - 7.7(10H)	3.29(12H, d)	15.6
$C_6H_5Ge[S_2P(OCH_3)_2]_3$	19	7.3 - 7.8(5H)	3.33(18H, d)	16.0

[a] The O-CH_3 peak of $NH_4S_2P(OCH_3)_2$ in D_2O appear at 3.93(d, J=14.7 Hz).

[b] All spectra were run in CS_2.

Number of expected protons and multiplicities in parentheses.

d = doublet, J = the coupling constant.

Table 22 ^1H nmr Data of *O,O'*-Diethyldithiophosphoric Acid Derivatives of Methyl and Phenylgermanes[a]

Compound	No.	Chemical Shift δ in ppm[b] Ge–CH_3/C_6H_5	OCH_2[c]	CH_3
$(CH_3)_3Ge[S_2P(OC_2H_5)_2]$	20	0.65(9H)	3.96(4H, q)	1.25(6H, t)
$(CH_3)_2Ge[S_2P(OC_2H_5)_2]_2$	21	1.21(6H)	4.07(8H, m)	1.25(12H, t)
$CH_3Ge[S_2P(OC_2H_5)_2]_3$	22	1.73(3H)	4.03(12H, m)	1.33(18H, t)
$(C_6H_5)_3Ge[S_2P(OC_2H_5)_2]$	23	7.1 – 7.6(15H)	3.70(4H, m)	0.89(6H, t)
$(C_6H_5)_2Ge[S_2P(OC_2H_5)_2]_2$	24	7.1 – 7.7(10H)	3.67(8H, m)	0.97(12H, t)
$C_6H_5Ge[S_2P(OC_2H_5)_2]_3$	25	7.2 – 7.9(5H)	4.03(12H, m)	1.17(18H, t)

[a] For $NH_4S_2P(OC_2H_5)_2$ in D_2O, the OCH_2 and CH_3 peaks appear at 3.98(m) and 1.22(t, J=7 Hz).

[b] All spectra were run in CS_2.
Number of expected protons and multiplicities in parentheses.
t = triplet, q = quartet, m = multiplet.

[c] Multiplets arising from doublet of quartets.

Table 23 ^{13}C nmr Data of *O,O'*-Dimethyldithiophosphoric Acid Derivatives of Methyl and Phenylgermanes[a]

		Chemical Shifts δ in ppm[b]		
Compound	No.	Ge-$\underline{C}H_3/\underline{C}_6H_5$	$O\underline{C}H_3$	$^2J_{POC}$ (Hz)
$(CH_3)_3Ge[S_2P(OCH_3)_2]$	13	3.2	53.3	–
$(CH_3)_2Ge[S_2P(OCH_3)_2]_2$	14	9.2	54.1	–
$CH_3Ge[S_2P(OCH_3)_2]_3$	15	13.7	54.4	–
$Cl_2Ge[S_2P(OCH_3)_2]_2$	16		54.8(d)	4.4
$Br_2Ge[S_2P(OCH_3)_2]_2$	16a		54.8(d)	4.4
$I_2Ge[S_2P(OCH_3)_2]_2$	16b		54.8(d)	4.4
$(C_6H_5)_3Ge[S_2P(OCH_3)_2]$	17	128.5, 130.3, 134.5, 135.0	58.6(d)	5.9
$(C_6H_5)_2Ge[S_2P(OCH_3)_2]_2$	18	128.4, 131.0, 134.7	54.0(d)	7.4
$C_6H_5Ge[S_2P(OCH_3)_2]_3$[c]	19	128.4, 128.8, 131.6, 132.0, 132.9, 133.8	54.5(d)	7.4

[a] The $O-\underline{C}H_3$ peak of $NH_4S_2P(OCH_3)_2$ in D_2O appears at 53.7(d, J=7.4 Hz).

[b] All spectra were recorded in $CDCl_3$.
Multiplicity in parentheses. d = doublet.

[c] For $\underline{C}_6H_5GeCl_3$ the signals are 129.7, 131.5, 133.2 and 135.2.

Table 24 ^{13}C nmr Data of *O,O'*-Diethyldithiophosphoric Acid Derivatives of Methyl and Phenylgermanes[b]

Compound	No.	Chemical Shifts δ in ppm[b] Ge–$\underline{C}H_3$/$\underline{C}_6H_5$	$O\underline{C}H_2$	$^2J_{POC}$ (Hz)	$\underline{C}H_3$
$(CH_3)_3Ge[S_2P(OC_2H_5)_2]$	20	3.6	63.6(d)	7.4	15.9
$(CH_3)_2Ge[S_2P(OC_2H_5)_2]_2$	21	9.3	64.2(d)	7.4	15.9
$CH_3Ge[S_2P(OC_2H_5)_2]_3$	22	15.9	64.6(d)	5.9	15.9
$(C_6H_5)_3Ge[S_2P(OC_2H_5)_2]$	23	128.5, 130.2, 134.7, 135.1	63.7(d)	5.9	15.7
$(C_6H_5)_2Ge[S_2P(OC_2H_5)_2]_2$	24	128.4, 128.8, 130.9, 131.4, 133.6, 134.4, 134.8	64.0(d)	5.9	15.5
$C_6H_5Ge[S_2P(OC_2H_5)_2]_3$	25	128.1, 128.6, 131.3, 131.9, 132.9, 134.0, 136.7	64.6(d)	4.4	15.8

a For $NH_4S_2P(OC_2H_5)_2$ in D_2O the O–$\underline{C}H_2$ and $\underline{C}H_3$ signals appear at 63.7(d, J=7.4 Hz) and 16.2 ppm respectively.

b All spectra were recorded in $CDCl_3$.

Table 25 ^{31}P nmr Data of Dithiophosphatogermanes[a]

Compound	No.	Chemical Shifts δ in ppm PS_2	$^3J_{POCH}$ (Hz)
$(CH_3)_3Ge[S_2P(OCH_3)_2]$	13	95.6	14.4
$(CH_3)_2Ge[S_2P(OCH_3)_2]_2$	14	91.3	15.0
$CH_3Ge[S_2P(OCH_3)_2]_3$	15	85.5, 87.3, 88.8	15.6
$Cl_2Ge[S_2P(OCH_3)_2]_2$	16	80.8, 82.7	16.2
$Br_2Ge[S_2P(OCH_3)_2]_2$	16a	85.2, 88.7	16.0
$I_2Ge[S_2P(OCH_3)_2]_2$	16b	86.3, 86.6	15.0
$(C_6H_5)_3Ge[S_2P(OCH_3)_2]$	17	94.1	15.0
$(C_6H_5)_2Ge[S_2P(OCH_3)_2]_2$	18	92.5	15.6
$C_6H_5Ge[S_2P(OCH_3)_2]_3$	19	87.4, 88.9, 90.1	16.0
$(CH_3)_3Ge[S_2P(OC_2H_5)_2]$	20	92.6	10.3
$(CH_3)_2Ge[S_2P(OC_2H_5)_2]_2$	21	86.2, 88.2	10.3
$CH_3Ge[S_2P(OC_2H_5)_2]_3$	22	80.4, 82.3, 84.1	10.3
$(C_6H_5)_3Ge[S_2P(OC_2H_5)_2]$	23	89.1	10.3
$(C_6H_5)_2Ge[S_2P(OC_2H_5)_2]_2$	24	86.4	10.3
$C_6H_5Ge[S_2P(OC_2H_5)_2]_3$	25	82.3, 84.2, 84.9	10.3

[a] For $NH_4S_2P(OCH_3)_2$ and $NH_4S_2P(OC_2H_5)_2$ in D_2O the signals appear at 95.6 (septet, J=14.7 Hz) and 111.0 (pentet, J=10.3 Hz) respectively.

Table 26 Vibrational Data of $(CH_3)_3Ge[S_2P(OCH_3)_2]$ (13), $(CH_3)_2Ge[S_2P(OCH_3)_2]_2$ (14) and $CH_3Ge[S_2P(OCH_3)_2]_3$ (15)

Compound 13		Compound 14		Compound 15		Assignment
IR (Neat)	Raman	IR (Neat)	Raman	IR (Neat)	Raman (cm^{-1})	
2994m	2977(14)	3002m		30001m	3015(11)	ν(C-H)
2957s	2938(30)	2954s	2942(99)	2957s	2945(59)	
2922m	2907(99)	2902sh	2914(90)	2902vw	2922(41)	
2851m	2836(17)	2851m	2838(45)	2850m	2838(24)	
1822wbr		1822wbr		1838wbr		
				1515vs		
1450s		1451s		1451s		
1402m		1400vw		1395vw		
1234s	1242(11)	1230w		1226vw		
1171s		1171s		1171s		
1038sh		1036sh		1033sh		
1008vsbr		1008vsbr		1001vsbr		ν(O-CH_3)
835vsbr		802vsbr	817(17)	805vsbr	812(10)	ν(PO_2)
798sh		792sh		750sh		ρ(Ge-CH_3)
655s	659(44)		657(100)	648vs	655(78)	ν(P=S)
609s	610(29)	638vs			609(15)	ν(Ge-C)as
568s	567(100)	579w	579(66)			ν(Ge-C)sym
527s	522(36)	521s	521(77)	517s	519(27)	ν(P-S)
490s	490(20)	488s	488(60)	480s	484(27)	
398s	398(15)	401s	404(75)	406s		ν(Ge-S)
366m	362(13)	368m	366(77)	376sh	388(100)	δ(POC)

Table 27 Vibrational Data[a] of $Cl_2Ge[S_2P(OCH_3)_2]_2$ (16), $Br_2Ge[S_2P(OCH_3)_2]_2$ (16a) and $I_2Ge[S_2P(OCH_3)_2]_2$ (16b)

Compound 16		Compound 16a		Compound 16b		Assignment
IR (Neat)	Raman	IR (Neat)	Raman	IR (Neat)	Raman (cm^{-1})	
3005w		3006w		3005m		
2961s	2947(43)	2958s	2945(29)	2958s	2946(18)	ν(C-H)
2855m	2841(18)	2851m	2843(11)	2851m	2840(9)	
1846wbr		1836wbr		1830wbr		
		1514s		1515w		
1450s		1440s		1450s		
1172s		1172s		1172s		
1025sh		1038sh		1038sh		
1005vsbr		1003vsbr		1004vsbr		ν(O-CH_3)
812vsbr	842(8)	814vsbr		808vsbr	821(8)	ν(PO_2)
635vs	645(100)	637vs	653(100)	635s	654(100)	ν(P=S)
514m		513s		515s		ν(P-S)
476s	477(10)	474s	480(9)	473s	481(8)	
426sbr	428(18)	406sbr	405(30)	405sbr	393(18)	ν(Ge-S)
382vw	385(67)		380(20)		372(26)	δ(POC)
	374(66)					ν(Ge-Cl)
			270(83)			ν(Ge-Br)
					237(24)	ν(Ge-I)

a s = strong, m = medium, w = weak, v = very, sh = shoulder, br= broad. Raman intensities in parentheses.

Table 28 Vibrational Data of $(C_6H_5)_3Ge[S_2P(OCH_3)_2]$ (17), $(C_6H_5)_2Ge[S_2P(OCH_3)_2]_2$ (18) and $C_6H_5Ge[S_2P(OCH_3)_2]_3$ (19)

Compound 17		Compound 18		Compound 19		Assignment
IR	Raman	IR	Raman	IR	Raman (cm^{-1})	
(CS_2)		(CS_2)		(CCl_4)		
3022vw	3048(85)	3030vw	3045(75)	3053sh	3049(21)	
2951m	2943(13)	2969m	2942(32)	2947s	2942(23)	ν(C-H)
2847w	2835(7)	2850w	2832(15)	2842w	2838(11)	
	1579(43)		1579(38)		1579(11)	
		(Nujol)		(Nujol)		
1534w		1536m		1512w		
1458m	1452(6)					
1428m		1420m		1431m		
1180m	1181(9)	1167m		1167s		
1088s	1085(12)	1083m		1078sh		
1010vsbr	1022(26)	1024sbr	1022(28)	1000vsbr	1019(13)	ν(O-CH_3)
999sh	997(100)	984sh	994(100)		992(32)	ν(Ge-C_6H_5)
806sbr		806s	792(13)	781s	812(13)	ν(PO_2)
730s		731s		732s		
691s		689m		687m		
671sh	664(19)		667(22)			
650s	641(48)	645s	648(80)		652(100)	ν(P=S)
526m		522m	526(39)	509s	524(22)	ν(P-S)
457s		458m		454m		
388s	392(10)	392m	385(56)	408m		ν(Ge-S),
	361(10)		371(36)	375m	370(50)	δ(POC)

Table 29. Vibrational Data of $(CH_3)_2Ge[S_2P(OC_2H_5)_2]$ (20), $(CH_3)_2Ge[S_2P(OC_2H_5)_2]_2$ (21) and $CH_3Ge[S_2P(OC_2H_5)_2]_3$ (22)

Compound 20		Compound 21		Compound 22		Assignment
IR (Neat)	Raman	IR (Neat)	Raman	IR (Neat)	Raman (cm^{-1})	
2994s	2976(29)	2999s		2996s		ν(C-H)
2945sh		2947sh	2959(30)	2948s	2961(14)	
2912m	2907(100)	2912m	2915(100)	2914m	2924(100)	
1735wbr		1815wbr		1807wbr		
1472m		1471m		1467m		
1458m			1450(7)	1436m		
1383s		1384s		1382s		
1255m		1255m				
1154m				1155s		
1091m	1091(11)	1092w	1093(14)	1091m	1094(17)	
1035sh	1053(13)	1035sh	1054(30)	1039s	1055(19)	$\nu(O-CH_2)$
1008sbr		1008sbr	1038(11)	1003sbr		
948sbr		958sbr		952sbr		
831sbr		847sh				
777sbr		786sbr		792sbr		$\nu(PO_2)$
	731(14)		732(30)		733(20)	
657s	651(88)	644sbr	654(56)	644vs	654(93)	ν(P=S)
608s	608(23)				606(12)	ν(Ge-C)as
566m	565(81)	584w	580(40)		557(14)	ν(Ge-C)sym
536s	524(38)	532s	525(54)	527s	526(53)	ν(P-S)
391m		381sbr		398sbr	381(60)	ν(Ge-S)

Table 30. Vibrational Data of $(C_6H_5)_2Ge[S_2P(OC_2H_5)_2]$ (23), $(C_6H_5)_2Ge[S_2P(OC_2H_5)_2]_2$ (24) and $C_6H_5Ge[S_2P(OC_2H_5)_2]_3$ (25)

Compound 23		Compound 24		Compound 25		Assignment
IR (CCl_4)	Raman	IR (Neat)	Raman	IR (Neat)	Raman (cm^{-1})	
3045sh	3025(75)	3061w	3051(54)	3067vw	3054(17)	ν(C-H)
2982w	2960(11)	2992s		2990s		
2928w	2924(11)	2946m	2926(36)	2949sh	2929(35)	
1556w	1578(37)	1518vs		1514m		
1474w		1468m		1472m		
1427sh		1429s		1431s		
1357s		1384s		1386s		
(Nujol)						
1301m		1301m		1298sh		
1151m	1149(12)	1154s		1154s		
1088m	1082(12)	1086s	1091(11)	1094s		
1005mbr	1020(23)	1006vsbr	1021(25)	1003vsbr	1019(10)	ν(O-CH_2)
991sh	995(100)	951vsbr	996(100)	962vsbr	995(6)	ν(Ge-C_6H_5)
776m		788vsbr		791vsbr		ν(PO_2)
735s	732(31)	732s		733s		
694m	661(25)	691s	666(40)	685s		
639mbr	647(39)	641vs	651(84)	640vs	652(100)	ν(P=S)
542w	555(33)	529s	528(16)	527s	535(9)	
508m	524(47)	502sh		492sh		ν(P-S)
458s		455s		451m		
376w		395sbr		398sbr	384(41)	ν(Ge-S)

Table 31 Mass Spectral Data[a] of $(CH_3)_3Ge[S_2P(OCH_3)_2]$ (13), $(CH_3)_2Ge[S_2P(OCH_3)_2]_2$ (14) and $CH_3Ge[S_2P(OCH_3)_2]_3$ (15)

Compound 13[b] (FI)	Compound 14 (EI)	Compound 15 (EI)	Fragment
		403(10.0)	$CH_3Ge[S_2P(OCH_3)_2]_2^+$
314(12.3)		314(9.8)	$[(CH_3O)_2PS_2]_2^{+\cdot}$
276(100)			$(CH_3)_3Ge[S_2P(OCH_3)_2]^{+\cdot}$
	261(100)		$(CH_3)_2Ge[S_2P(OCH_3)_2]^+$
		231(9.8)	$Ge[S_2P(OCH_3)_2]^+$
	158(6.1)	158(60.8)	$(CH_3O)_2PS_2H^{+\cdot}$
157(7.5)	157(4.4)		$(CH_3O)_2PS_2^+$
	136(17.6)		$(CH_3)_2GeS^{+\cdot}$
	125(39.4)	125(100)	$(CH_3O)_2PS^+$
119(41)			$(CH_3)_3Ge^+$
	93(35.4)	93(45.3)	$(CH_3O)_2P^+$

a Relative abundances in parentheses.

b Association peaks corresponding to m/z 433 ($(CH_3)_3Ge-[S_2P(OCH_3)_2]_3^+$) and m/z 471 ($[(CH_3O)_2PS_2]_3^+$) were also observed.

Table 32 Mass Spectral Data of $Cl_2Ge[S_2P(OCH_3)_2]_2$ (16), $Br_2Ge[S_2P(OCH_3)_2]_2$ (16a) and $I_2Ge[S_2P(OCH_3)_2]_2$ (16b)

Compound 16 (FI)	Compound 16a (FI)	Compound 16b (EI)	Fragment
	546(1.4)		$Br_2Ge[S_2P(OCH_3)_2]_2^{+\cdot}$
		515(4.3)	$IGe[S_2P(OCH_3)_2]_2^+$
		485(28.3)	$I_2Ge[S_2P(OCH_3)_2]^+$
	467(3.9)		$BrGe[S_2P(OCH_3)_2]^+$
458(2.8)			$Cl_2Ge[S_2P(OCH_3)_2]_2^{+\cdot}$
		455(7.6)	GeI_3^+
388(3.2)	388(29.1)	388(6.4)	$Ge[S_2P(OCH_3)_2]_2^{+\cdot}$
336(92.4)			$Cl_3Ge[S_2P(OCH_3)_2]^{+\cdot}$
314(100)	314(100)	314(17.2)	$[(CH_3O)_2PS_2]_2^{+\cdot}$
282(21.1)	282(29.2)		$[(CH_3O)_2PS]_2S^{+\cdot}$
		231(51.6)	$Ge[S_2P(OCH_3)_2]^+$
	218(25.2)		$[(CH_3O)_2P]_2S^{+\cdot}$
	172(45.9)		$(CH_3O)_2PS_2CH_3^{+\cdot}$
158(63.4)	158(22.0)		$(CH_3O)_2PS_2H^{+\cdot}$
		157(17.4)	$(CH_3O)_2PS_2^+$
		125(100)	$(CH_3O)_2PS^+$
		93(71.3)	$(CH_3O)_2P^+$
		63(21.2)	PO_2^+

Table 33 Mass Spectral Data of $(C_6H_5)_3Ge[S_2P(OCH_3)_2]$ (17), $(C_6H_5)_2Ge[S_2P(OCH_3)_2]_2$ (18) and $C_6H_5Ge[S_2P(OCH_3)_2]_3$ (19)

Compound 17 (EI)	Compound 18 (FI)	Compound 19 (EI)	Fragment
		625(1.3)	$C_6H_5Ge[S_2P(OCH_3)_2]_3^{+\cdot}$
		468(25.1)	$C_6H_5Ge[S_2P(OCH_3)_2]_2^{+}$
462(32.8)			$(C_6H_5)_3Ge[S_2P(OCH_3)_2]^{+\cdot}$
385(90.4)	385(54.7)		$(C_6H_5)_2Ge[S_2P(OCH_3)_2]^{+}$
	314(56.4)		$[(CH_3O)_2PS_2]_2^{+\cdot}$
308(100)			$C_6H_5Ge[S_2P(OCH_3)_2]^{+\cdot}$
	261(52.6)		$(C_6H_5)_2GeSH^{+}$
260(15.0)			$(C_6H_5)_2GeS^{+\cdot}$
		231(13.1)	$Ge[S_2P(OCH_3)_2]^{+}$
228(15.6)			$(C_6H_5)_2Ge^{+}$
		203(21.7)	$Ge[S_2P(OH)_2]^{+}$
	172(89.0)	172(27.9)	$(CH_3O)_2PS_2CH_3^{+\cdot}$
		158(6.4)	$(CH_3O)_2PS_2H^{+\cdot}$
	157(100)	157(8.1)	$(CH_3O)_2PS_2^{+}$
154(24.2)			$(C_6H_5)_2^{+\cdot}$
		151(4.4)	$C_6H_5Ge^{+}$
125(23.1)	125(14.1)	125(100)	$(CH_3O)_2PS^{+}$
93(15.8)		93(91.0)	$(CH_3O)_2P^{+}$

Table 34 Mass Spectral Data of $(CH_3)_3Ge[S_2P(OC_2H_5)_2]$ (20), $(CH_3)_2Ge[S_2P(OC_2H_5)_2]_2$ (21) and $CH_3Ge[S_2P(OC_2H_5)_2]_3$ (22)

Compound 20 (FI)	Compound 21 (FI)	Compound 22 (FI)	Fragment
	659(2.6)		$(CH_3)_2Ge[S_2P(OC_2H_5)_2]_3^+$
555(2.7)	555(6.7)		$[(C_2H_5O)_2PS_2]_3^+$
489(20.4)			$(CH_3)_3Ge[S_2P(OC_2H_5)_2]_2^+$
	474(21.0)		$(CH_3)_2Ge[S_2P(OC_2H_5)_2]_2^+\cdot$
		459(41)	$CH_3Ge[S_2P(OC_2H_5)_2]_2^+$
370(17.3)	370(19.1)		$[(C_2H_5O)_2PS_2]_2^+\cdot$
304(98.7)			$(CH_3)_3Ge[S_2P(OC_2H_5)_2]^+\cdot$
	289(100)		$(CH_3)_2Ge[S_2P(OC_2H_5)_2]^+$
		186(100)	$(C_2H_5O)_2PS_2H^+\cdot$
185(36.2)	185(46.7)	185(83.0)	$(C_2H_5O)_2PS_2^+$
153(4.6)	153(12.7)		$(C_2H_5O)_2PS^+\cdot$
121(100)	121(46.5)		$(C_2H_5O)_2P^+$

Table 35 Mass Spectral Data of $(C_6H_5)_3Ge[S_2P(OC_2H_5)_2]$ (23), $(C_6H_5)_2Ge[S_2P(OC_2H_5)_2]_2$ (24) and $C_6H_5Ge[S_2P(OC_2H_5)_2]_3$ (25)

Compound 23 (FI)	Compound 24 (FI)	Compound 25 (FI)	Fragment
		521(4.5)	$C_6H_5Ge[S_2P(OC_2H_5)_2]_2^+$
490(100)			$(C_6H_5)_3Ge[S_2P(OC_2H_5)_2]^+$
	413(58.0)		$(C_6H_5)_2Ge[S_2P(OC_2H_5)_2]^+$
370(3.3)	370(20.0)		$[(C_2H_5O)_2PS_2]_2^+$
	338(38.3)		$[(C_2H_5O)_2PS]_2S^+$
306(46.7)			$[(C_2H_5O)_2PS]_2^+$
		260(72.3)	$HGe[S_2P(OC_2H_5)_2]^+$
	214(100)		$(C_2H_5O)_2PS_2C_2H_5^+$
		186(100)	$(C_2H_5O)_2PS_2H^+$
185(10.5)	185(64.3)		$(C_2H_5O)_2PS_2^+$
	153(15.9)		$(C_2H_5O)_2PS^+$

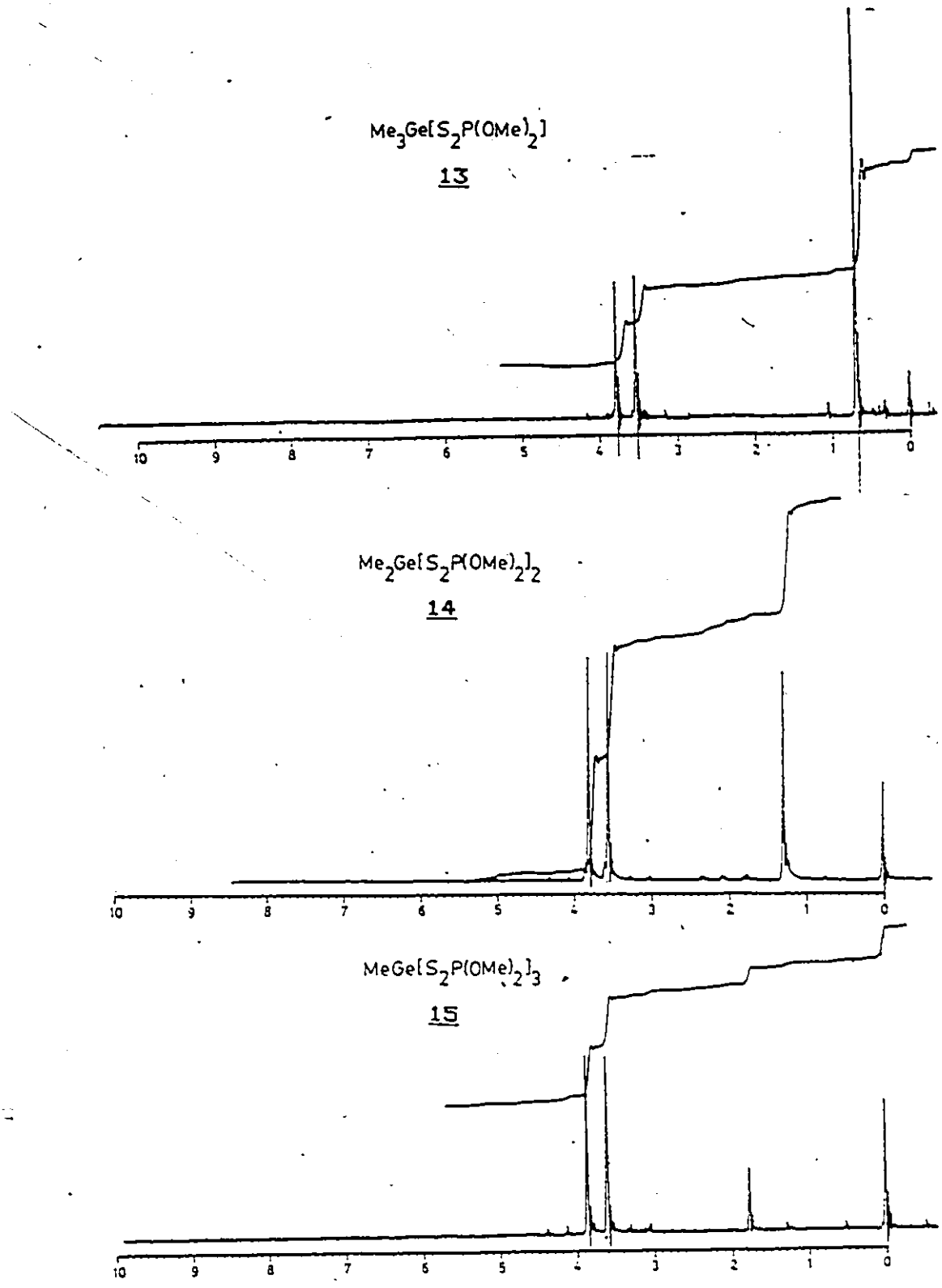
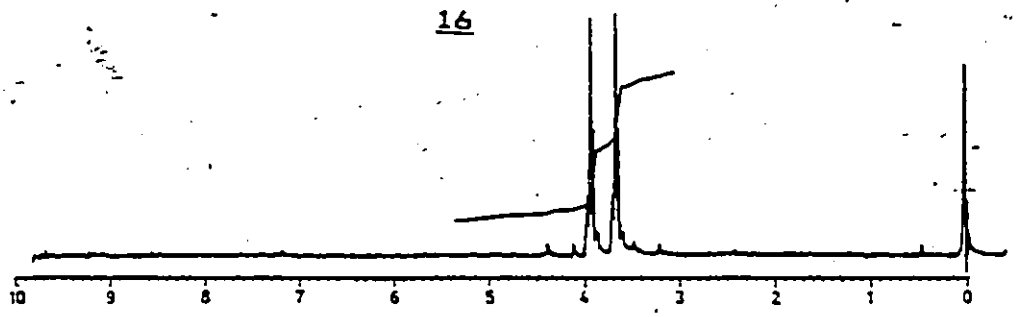


Figure 25 ^{1}H nmr Spectra of Compounds 13, 14 and 15.

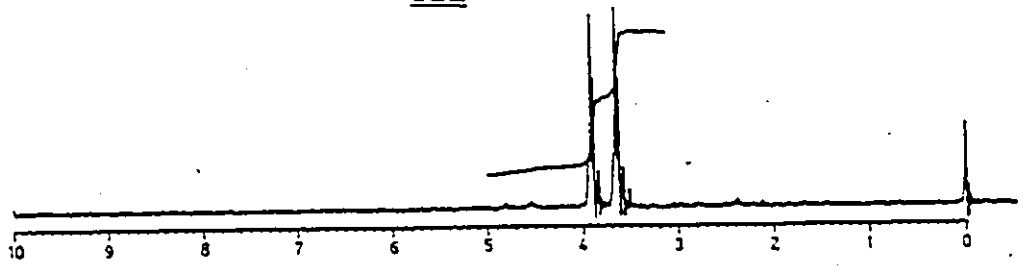
$Cl_2Ge[S_2P(OMe)_2]_2$

16



$Br_2Ge[S_2P(OMe)_2]_2$

16a



$I_2Ge[S_2P(OMe)_2]_2$

16b

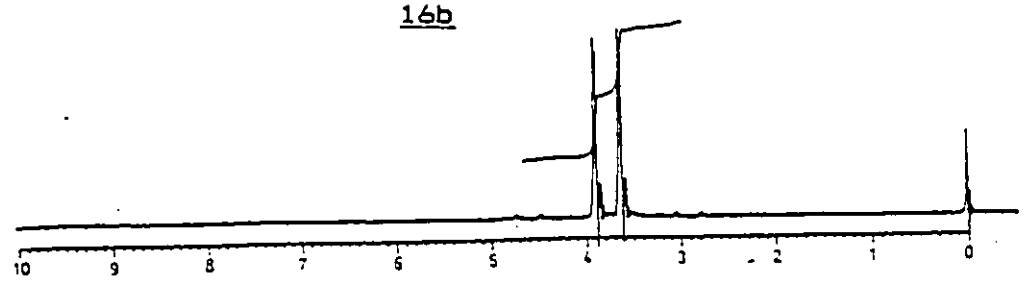


Figure 26 ^1H nmr Spectra of Compounds 16, 16a and 16b.

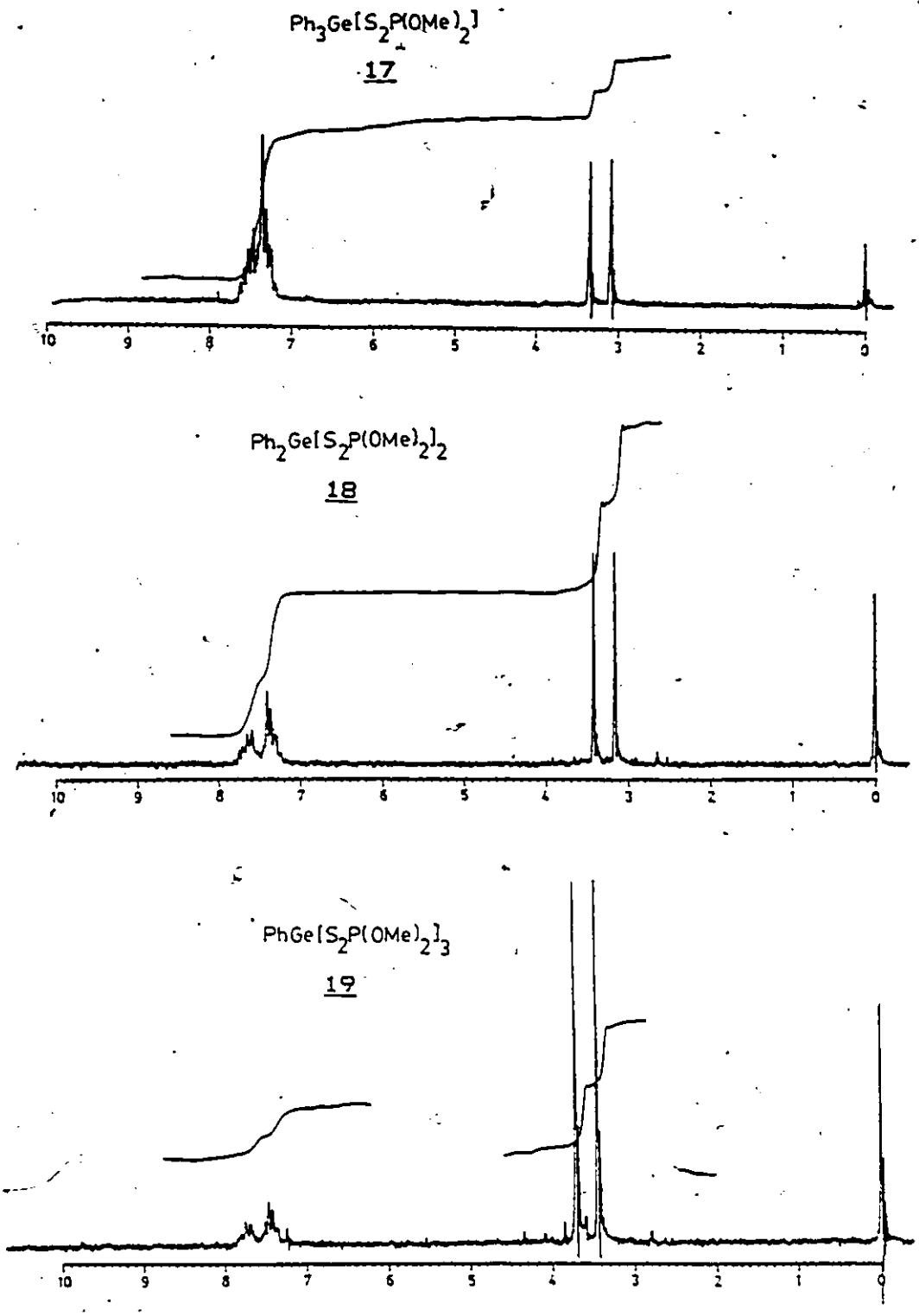


Figure 27 ^1H nmr Spectra of Compounds 17, 18 and 19.

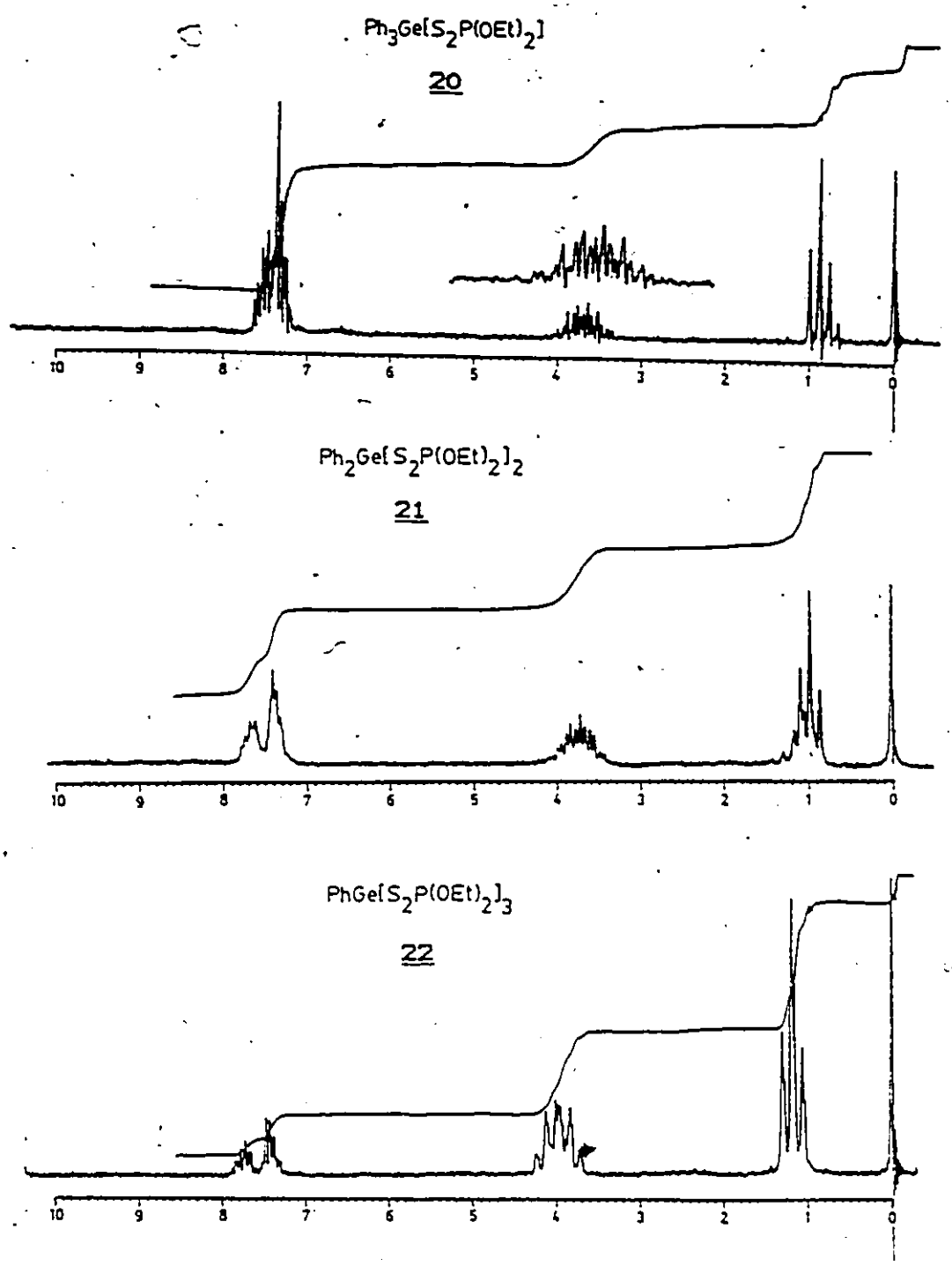


Figure 28 ^1H nmr Spectra of Compounds 20, 21 and 22.

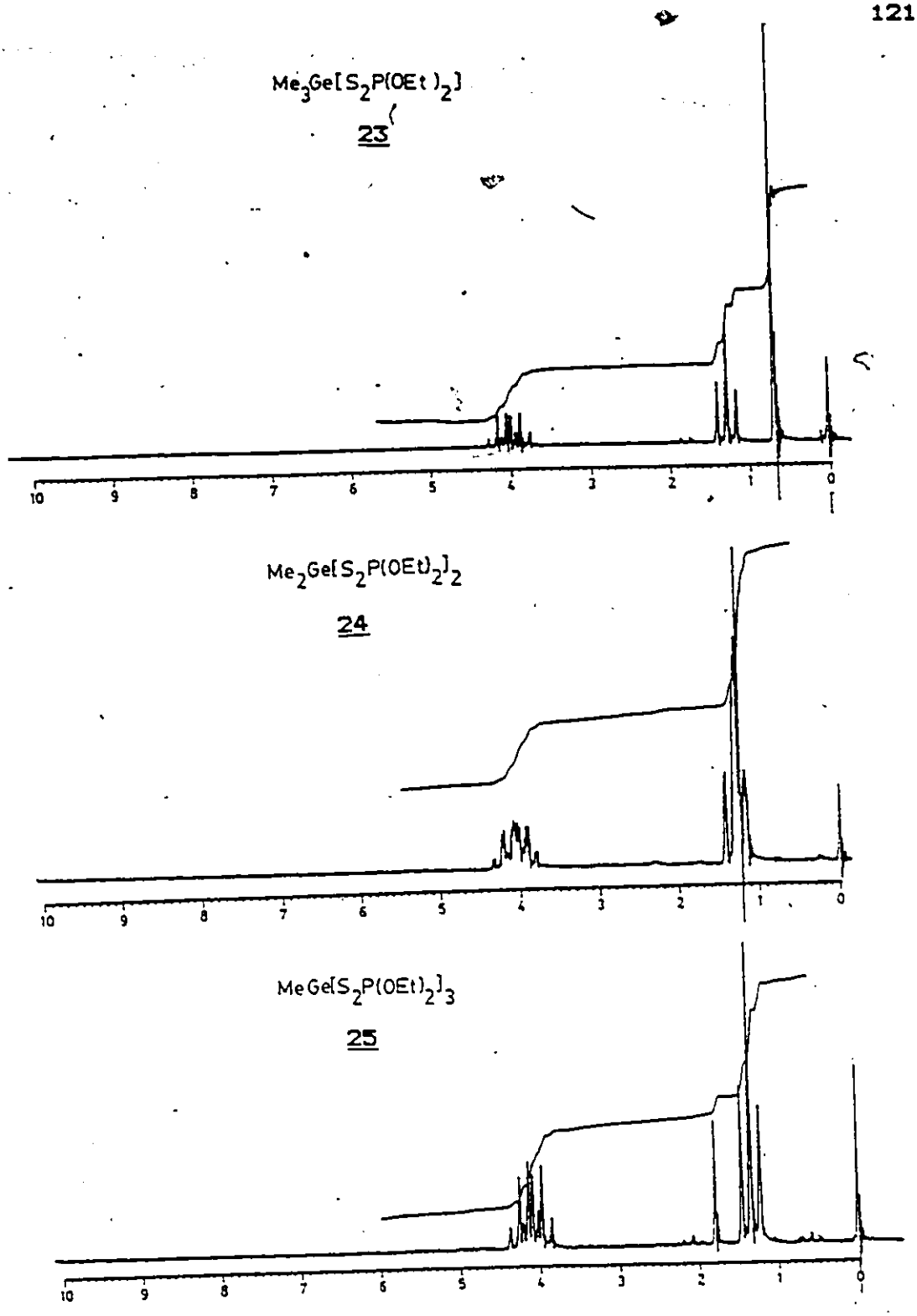
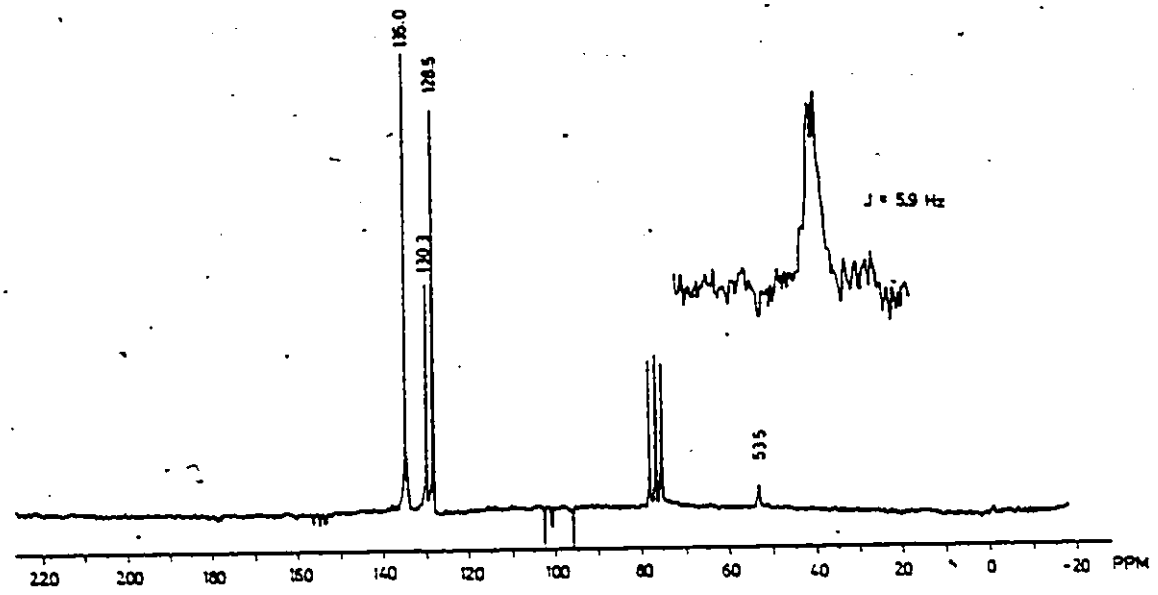


Figure 29. ^1H nmr Spectra of Compounds 23, 24 and 25.

$Ph_3Ge[S_2P(OMe)_2]$

14



$Me_2Ge[S_2P(OMe)_2]_2$

17

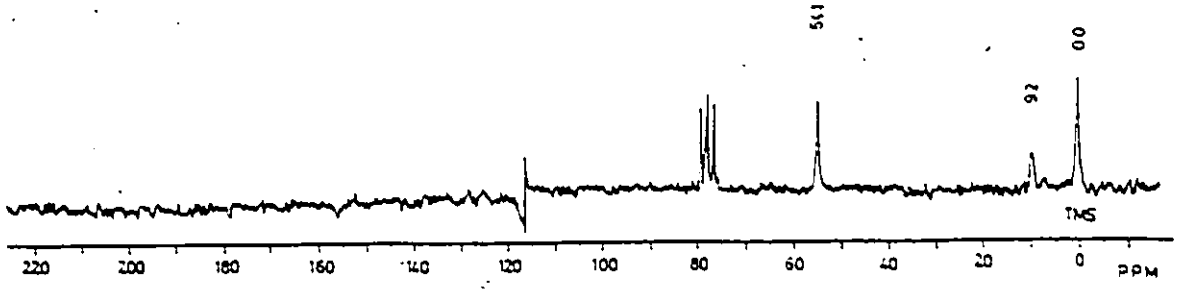
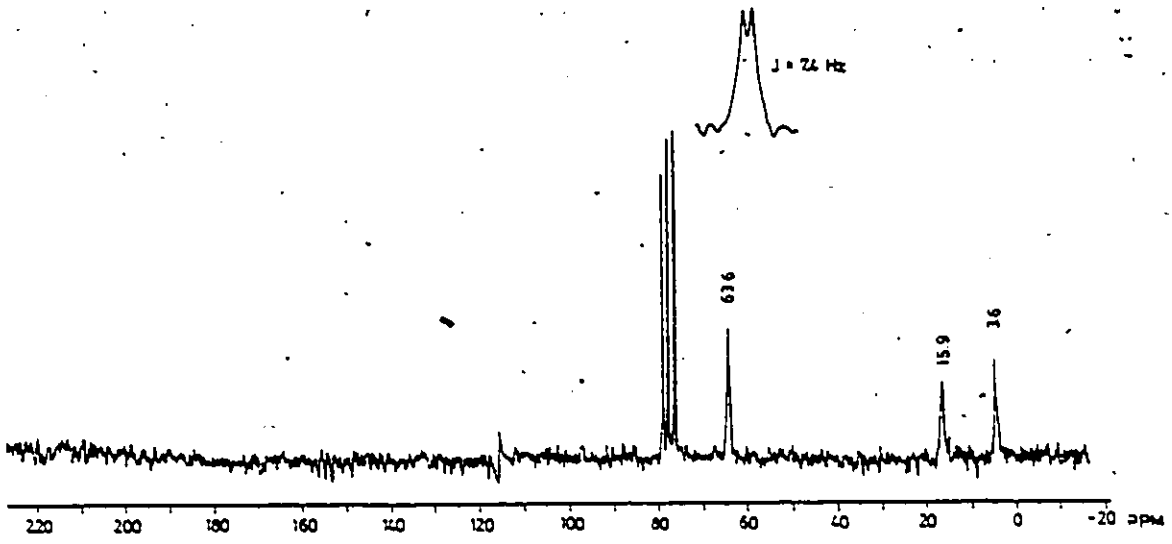


Figure 30 ^{13}C nmr Spectra of Compounds 14 and 17.

$Me_3Ge[S_2P(OEt)_2]$

20



$Ph_2Ge[S_2P(OEt)_2]_2$

24

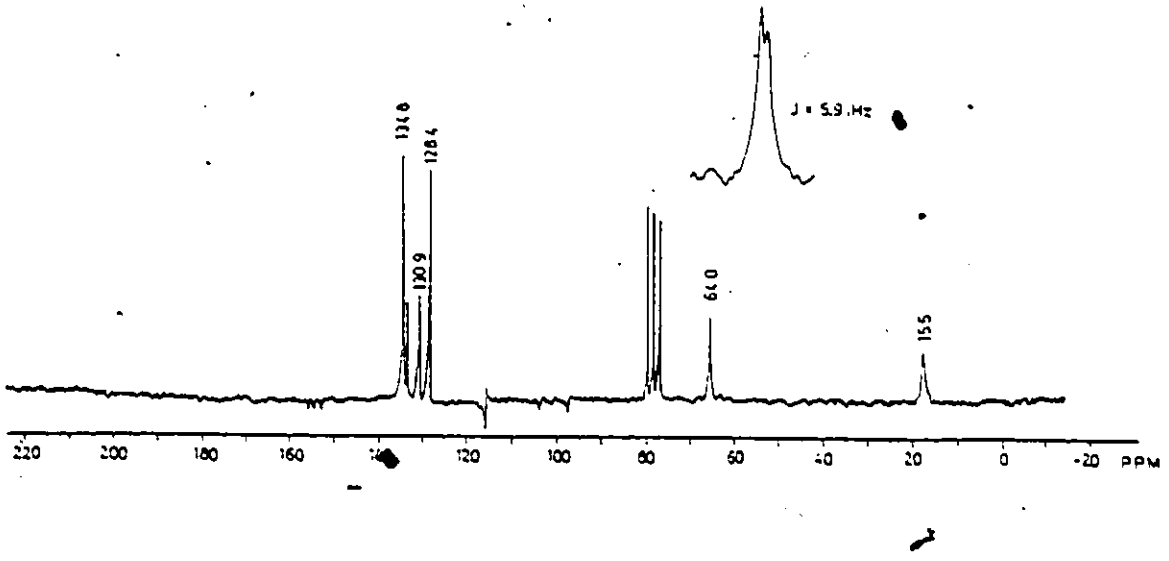
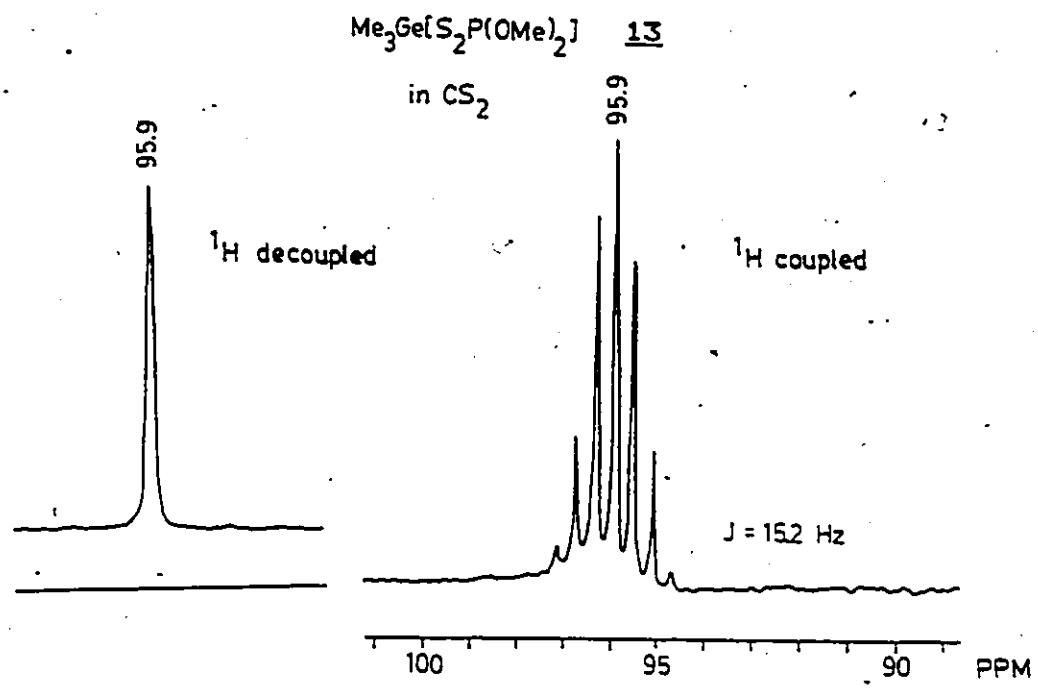


Figure 31 ^{13}C nmr Spectra of Compounds 20 and 24.



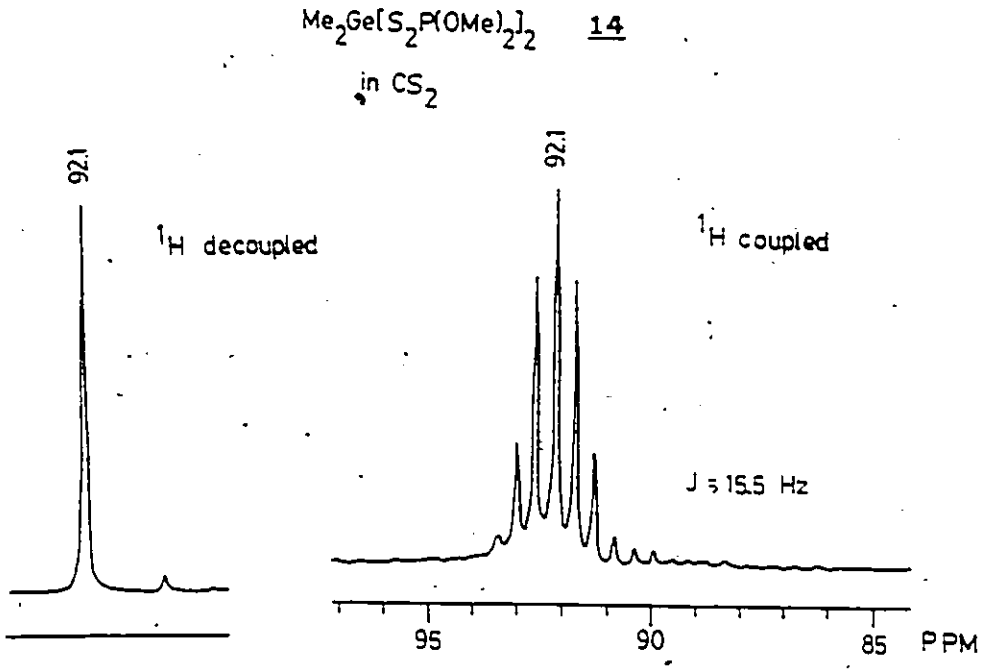


Figure 32 ^{31}P nmr Spectra of Compounds 13 and 14.

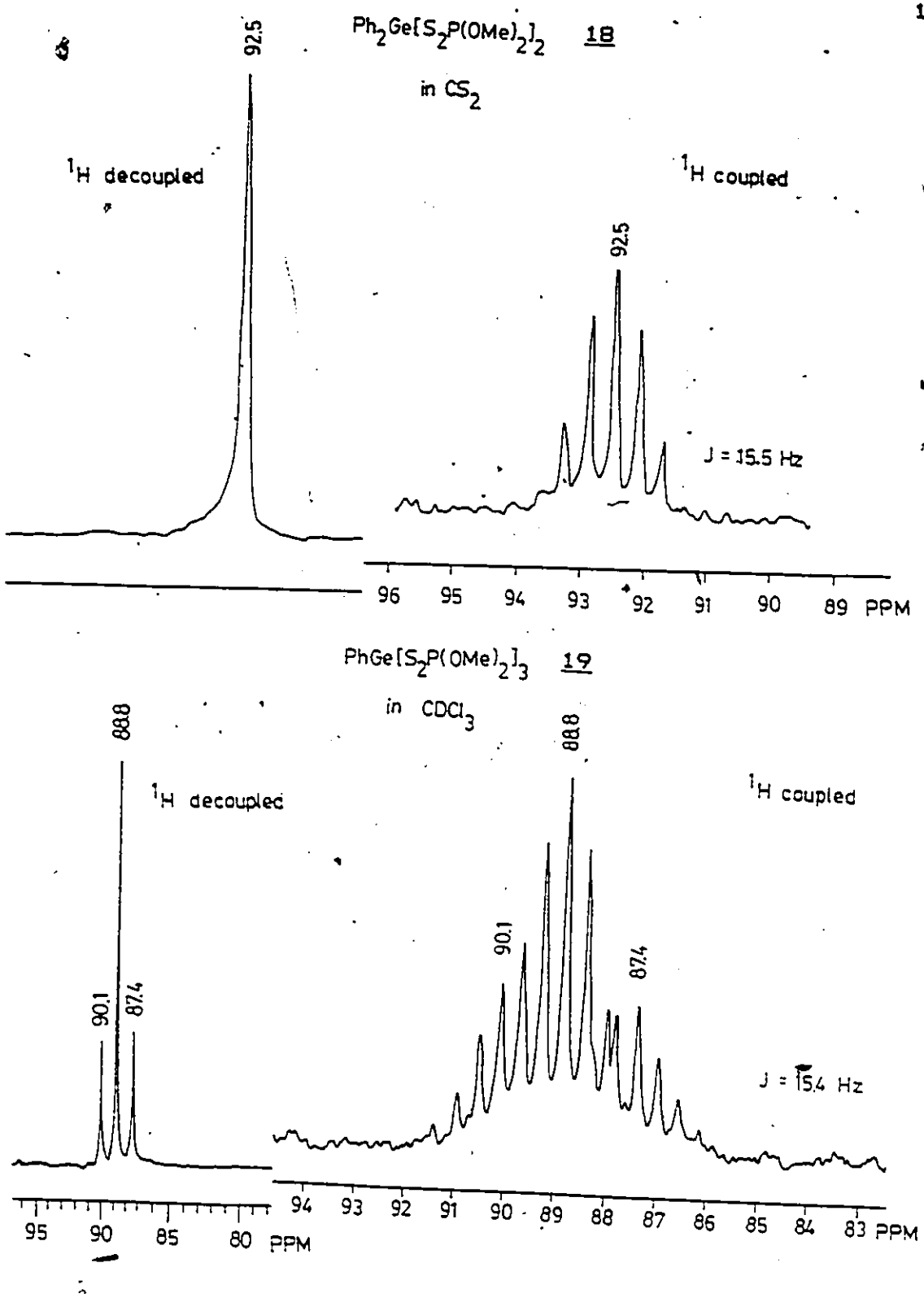


Figure 33 ^{31}P nmr Spectra of Compounds 18 and 19.

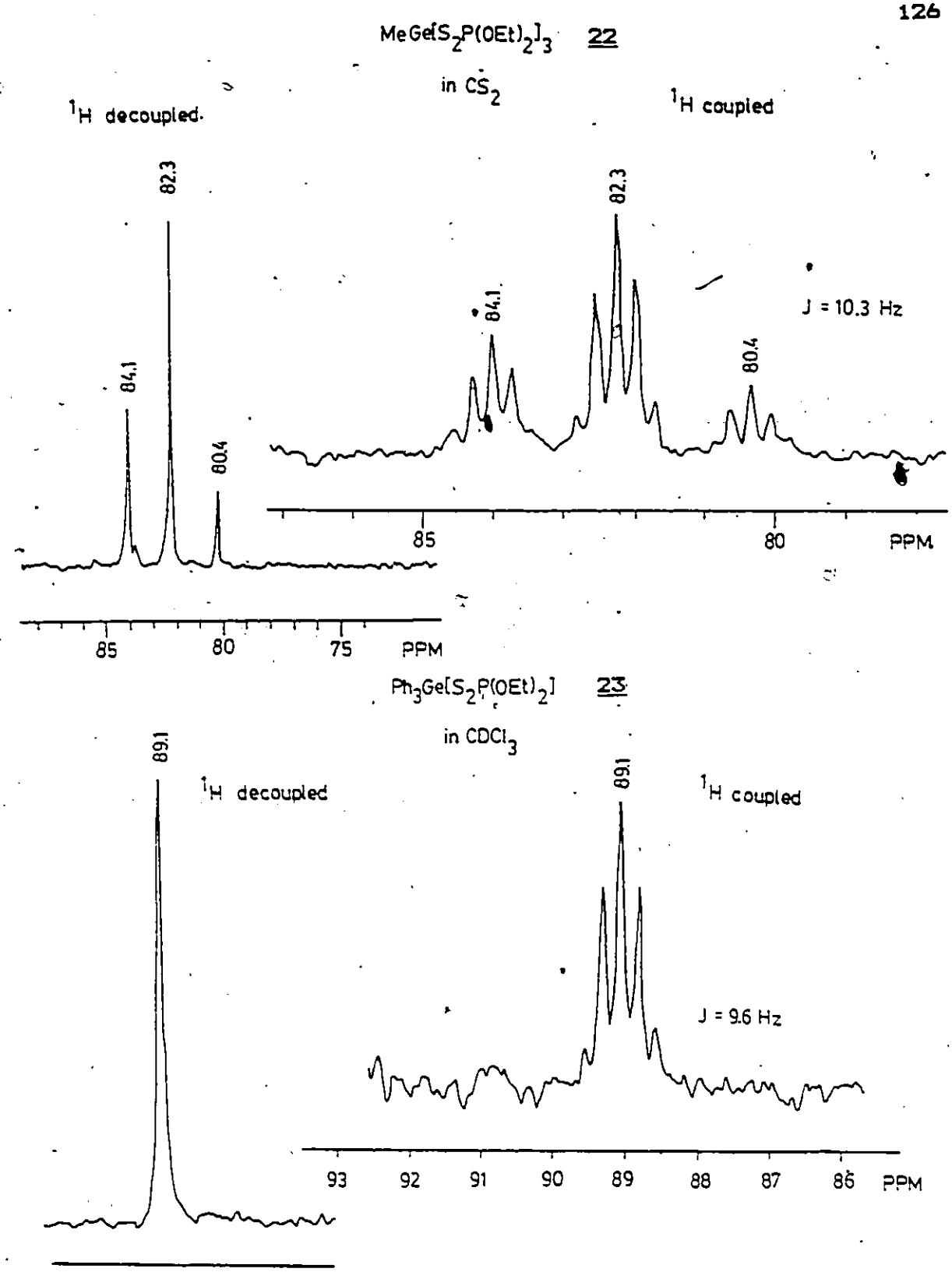


Figure 34 ^{31}P nmr Spectra of Compounds 22 and 23.

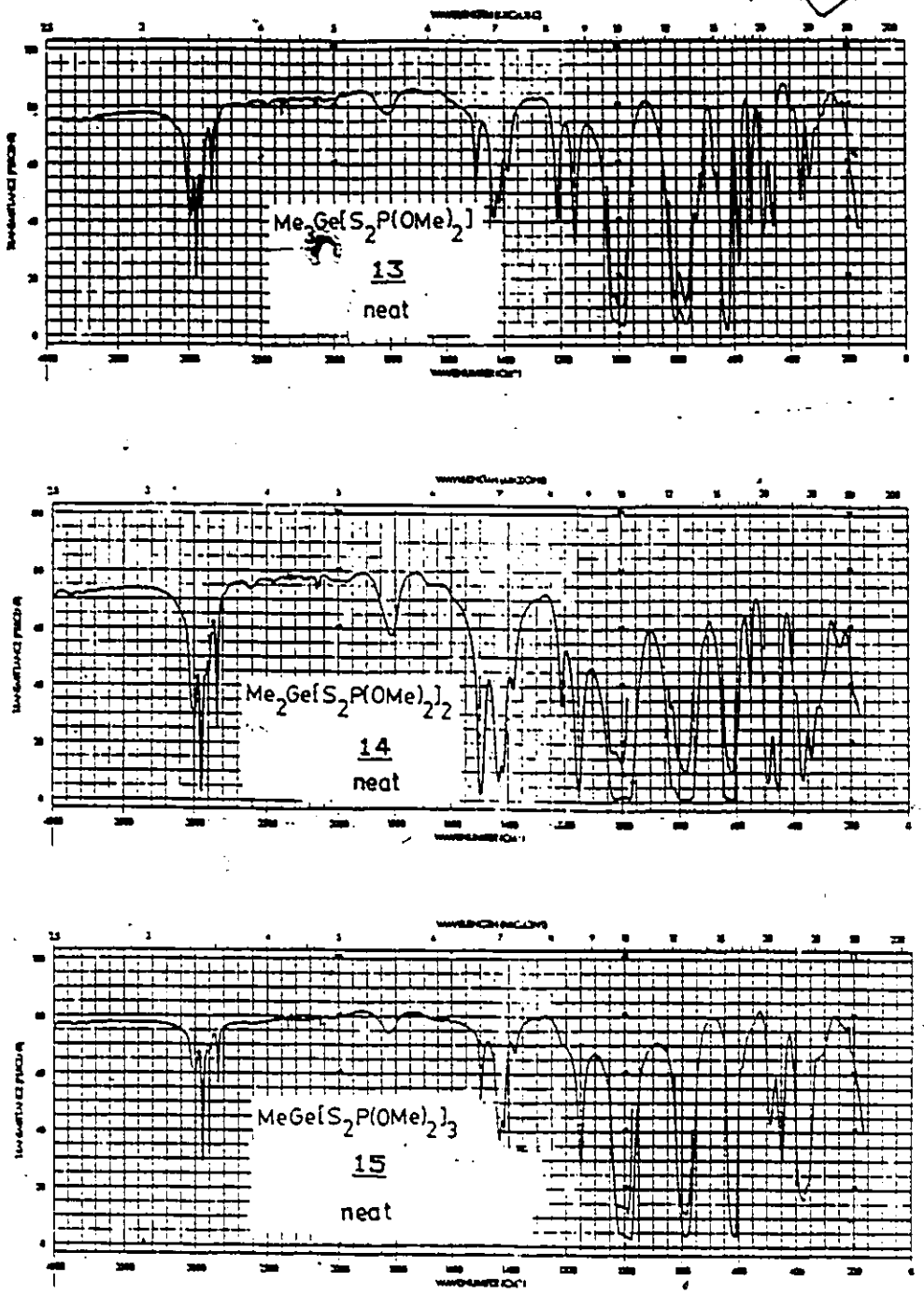


Figure 35 Infrared Spectra of Compounds 13, 14 and 15.

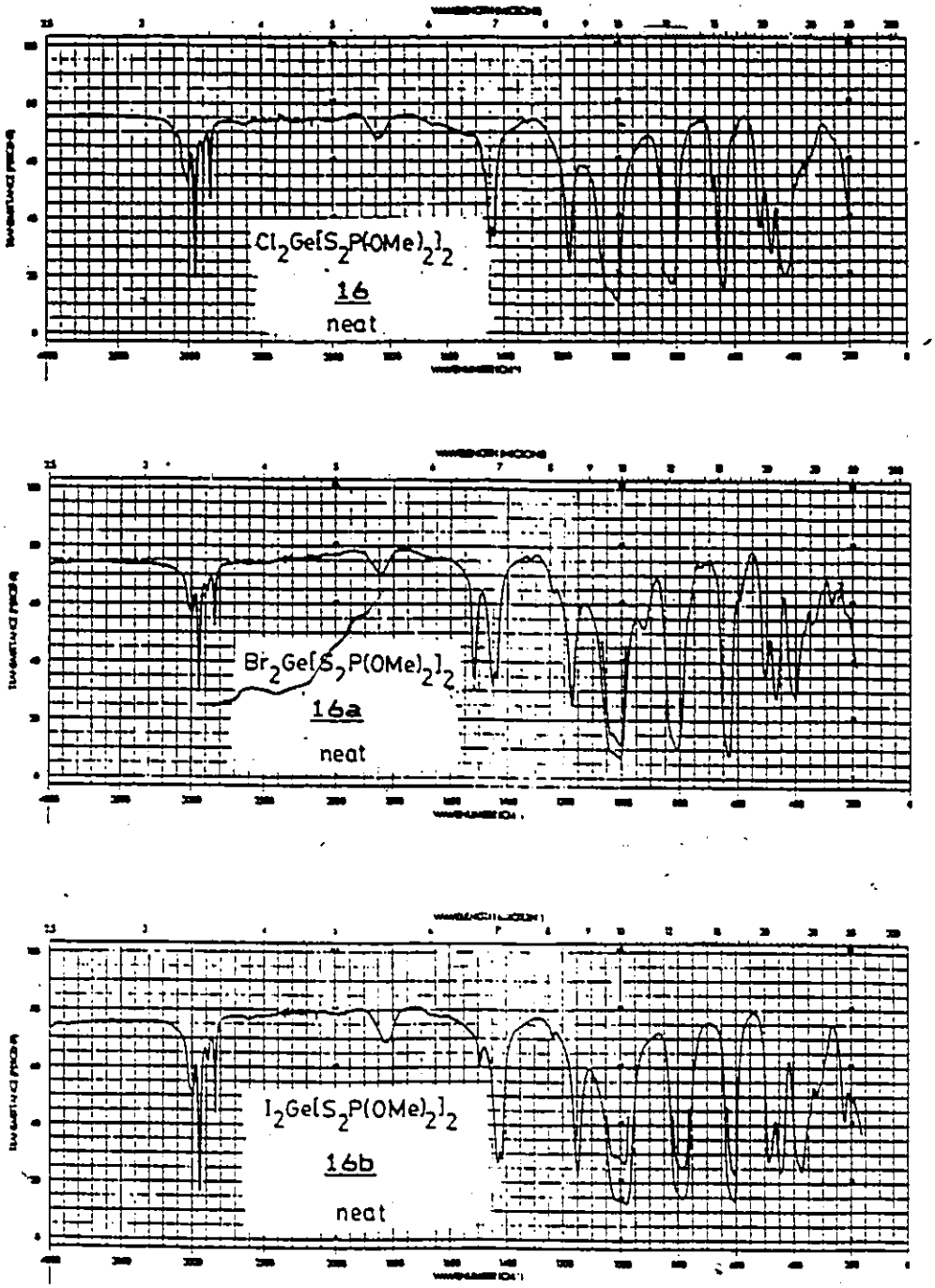


Figure 36 Infrared Spectra of Compounds 16, 16a and 16b.

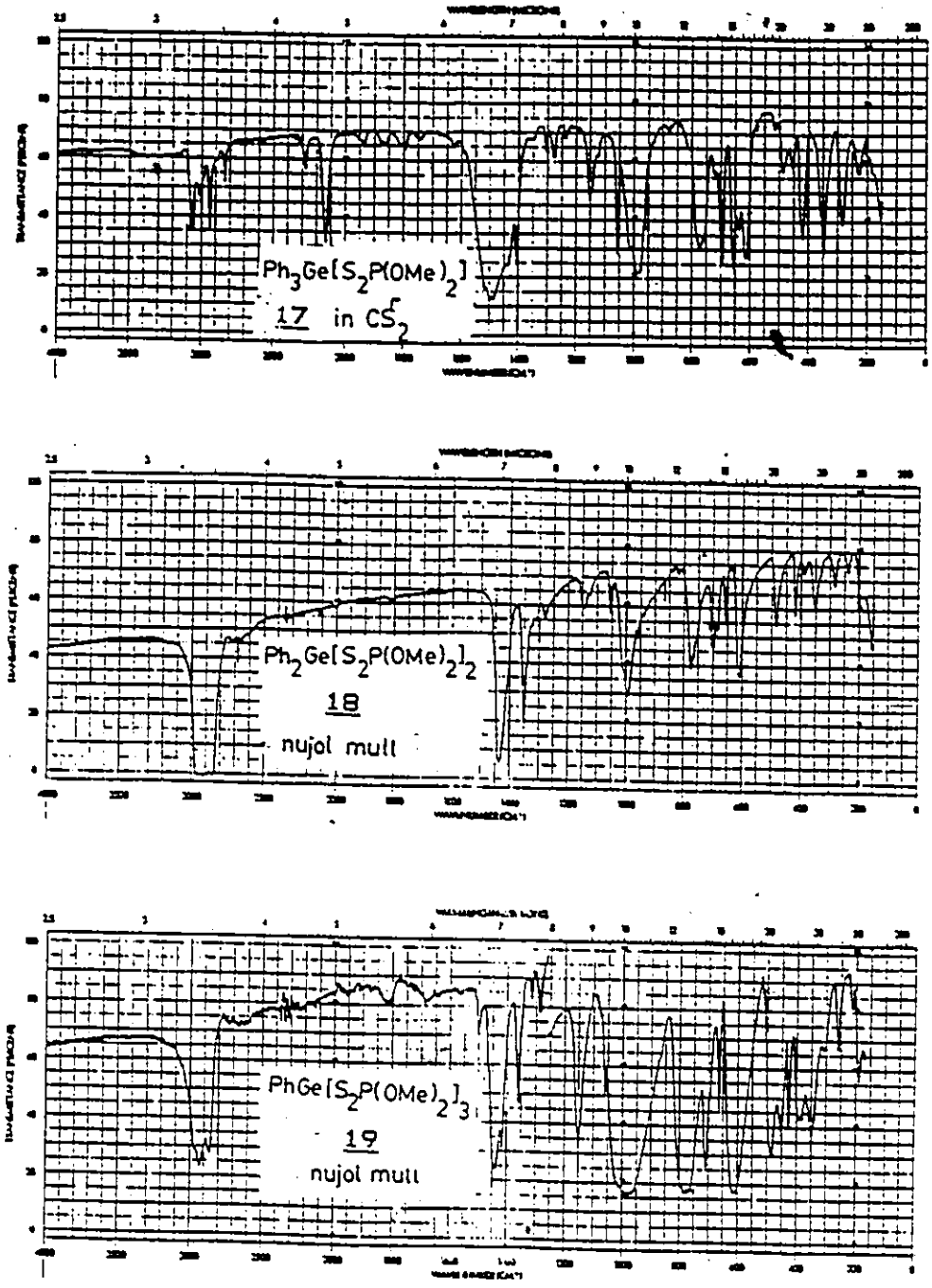


Figure 37 Infrared Spectra of Compounds 17, 18 and 19.

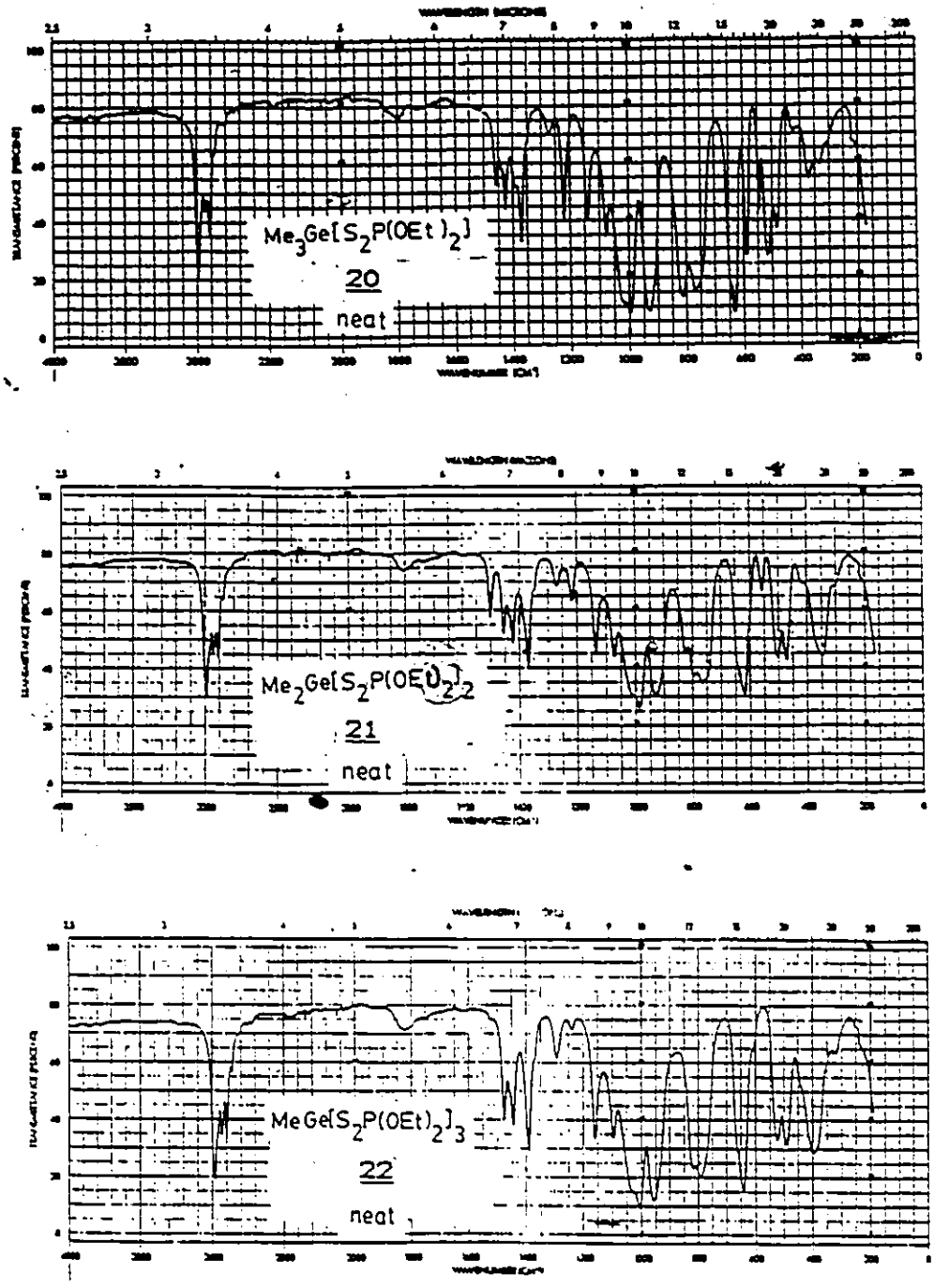
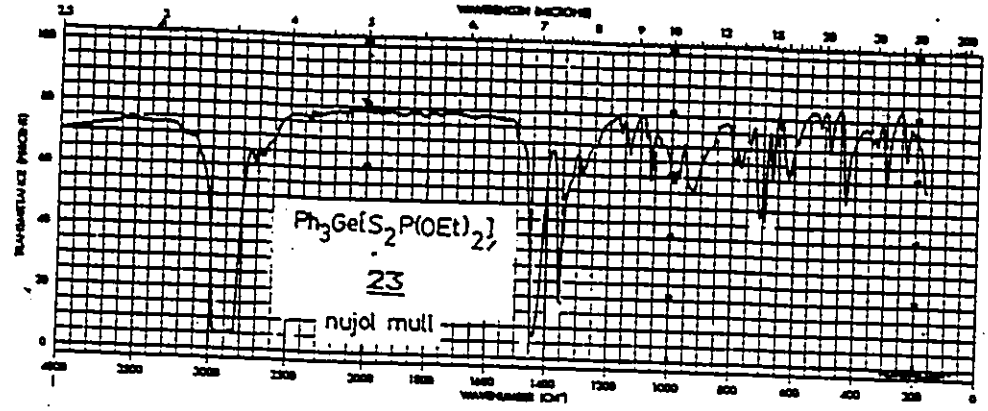
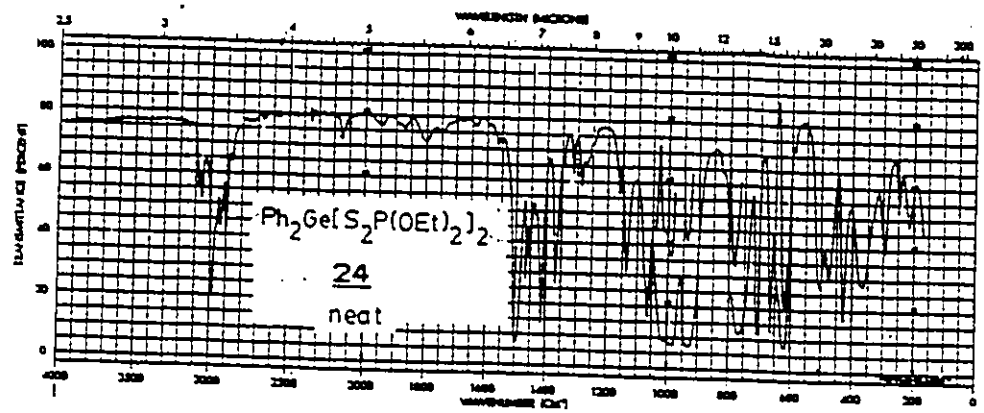


Figure 38 Infrared Spectra of Compounds 20, 21 and 22.





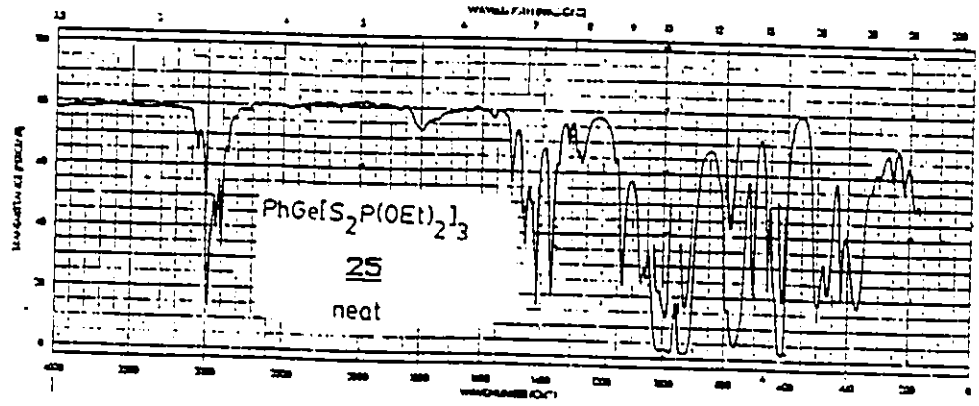


Figure 39 Infrared Spectra of Compounds 23, 24 and 25.

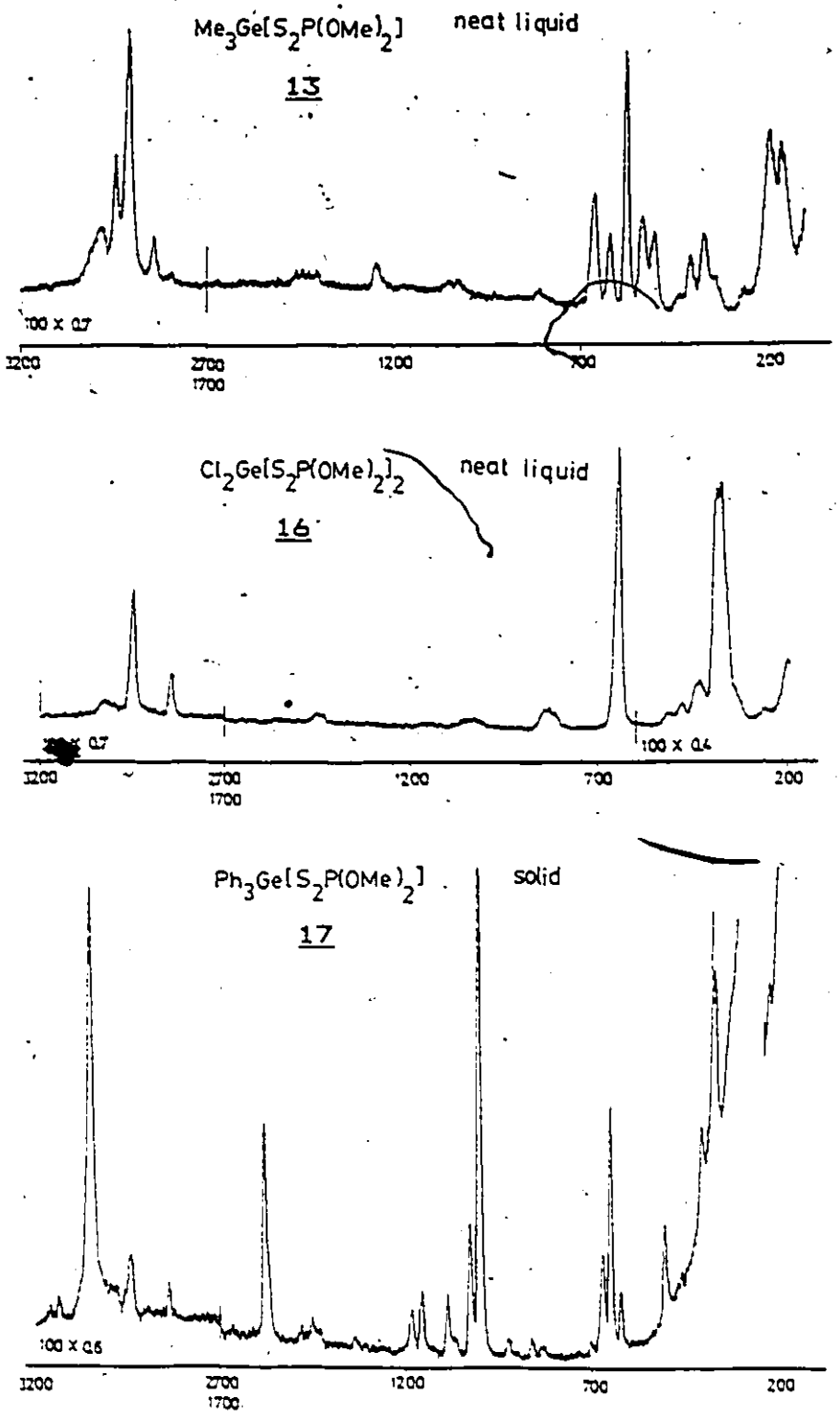
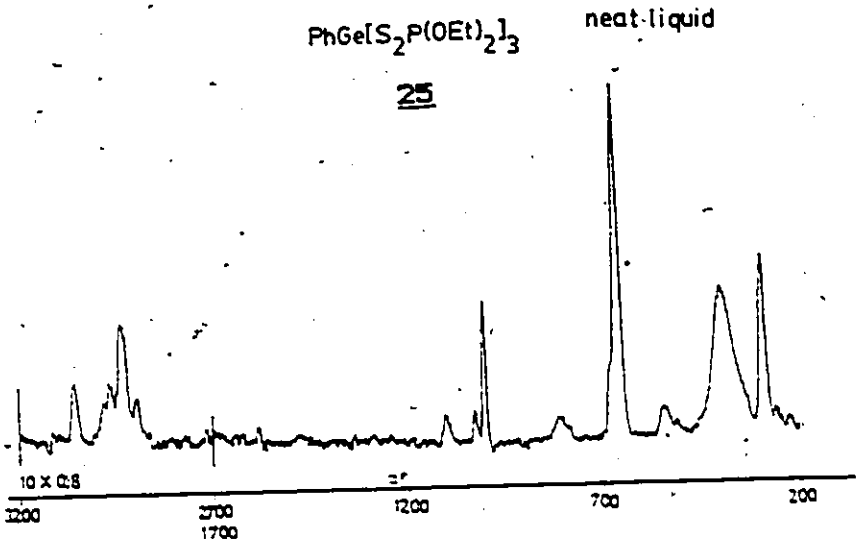


Figure 40 Raman Spectra of Compounds 13, 16 and 17.



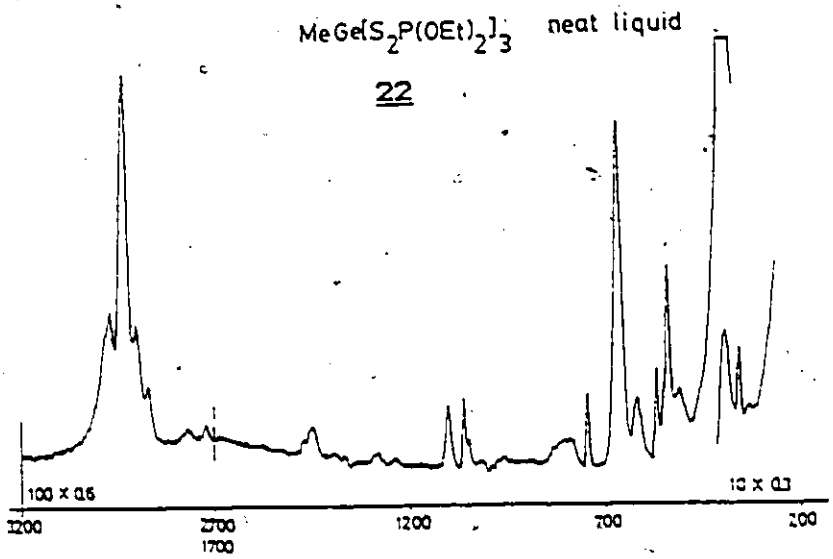


Figure 41 Raman Spectra of Compounds 22 and 25.

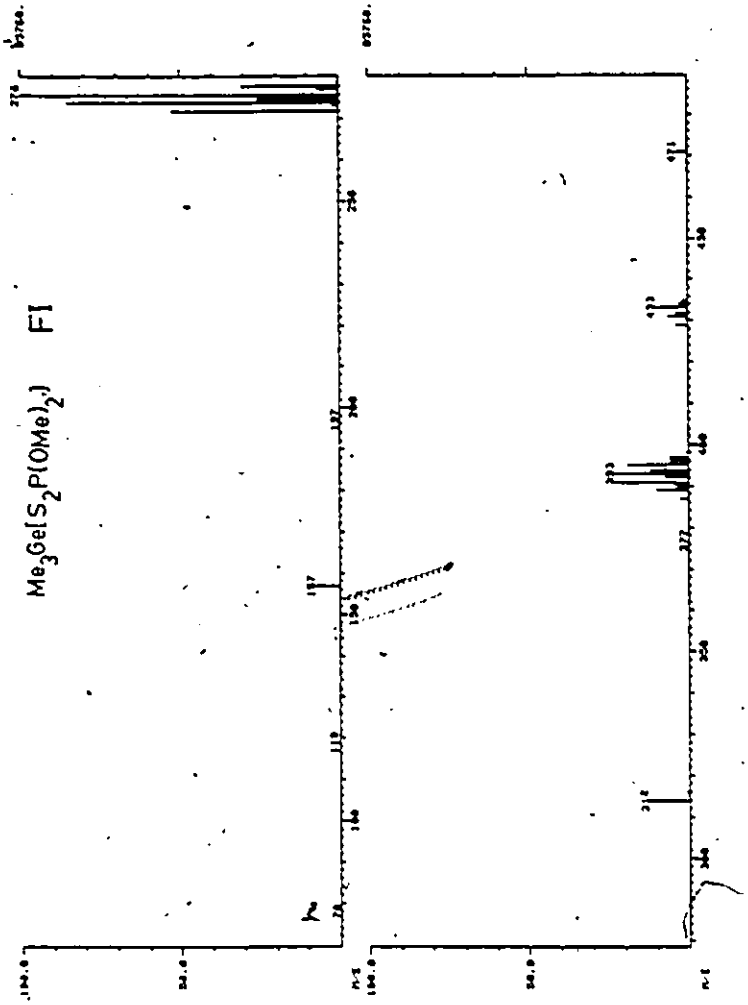
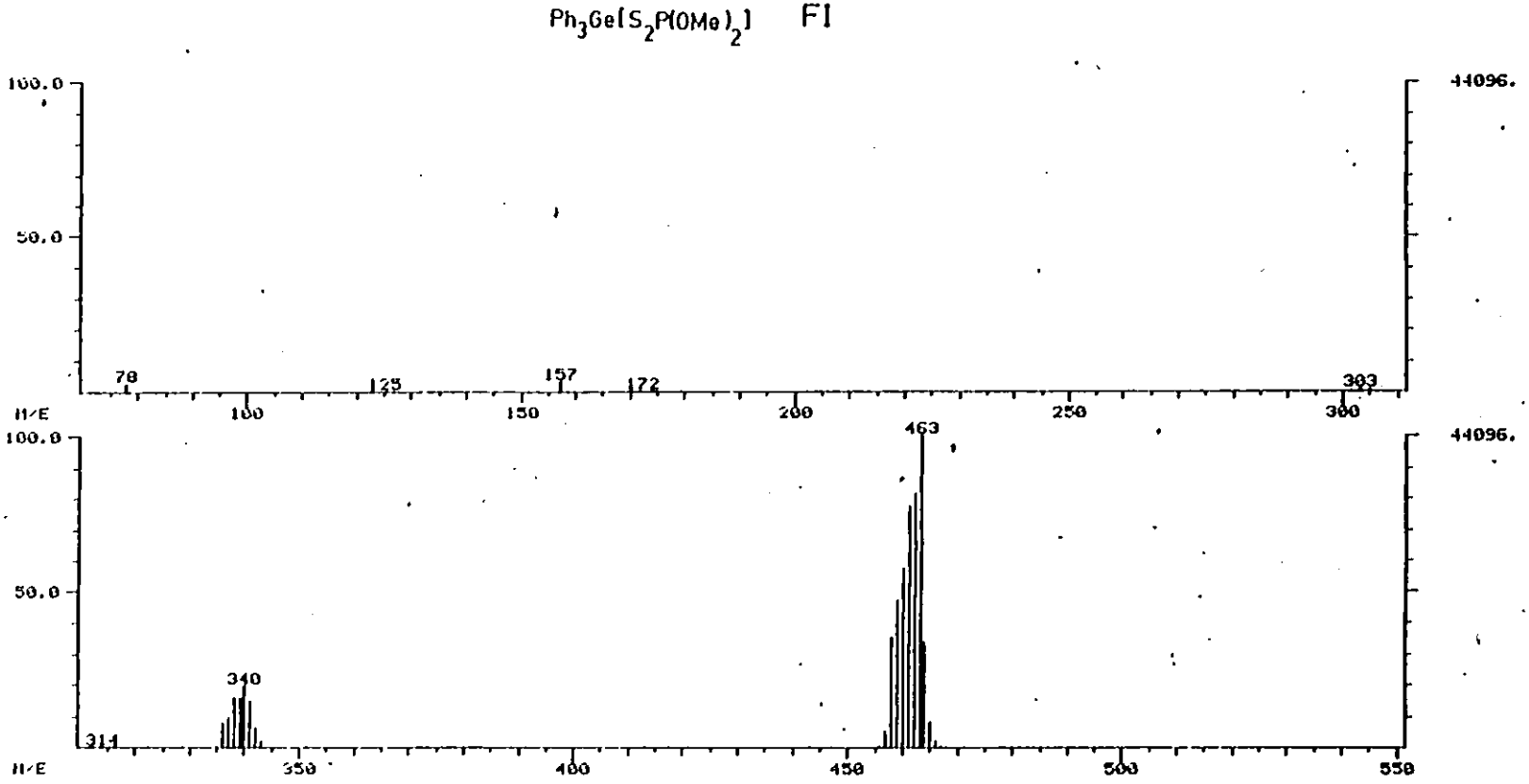


Figure 42 Field Ionization Mass Spectrum of Compound 13.

Figure 43 Field Ionization Mass Spectrum of Compound 17.



CHAPTER VIII

CRYSTAL STRUCTURES OF ORGANOGERMANIUM DITHIOCARBAMATES AND DITHIOPHOSPHATES

Metallic dithiophosphates and dithiocarbamates represent a fascinating array of molecules and nowhere is it more apparent than in their structural diversities. In addition to being monodentate, bidentate or bridging, the ligands add unexpected dimensions to molecules. For example, in $Cu_4[SP(S)(OC_3H_7\text{-}i)_2]_4$, the copper atoms form a tetrahedron and the dithiophosphate groups coordinate from the faces.[19] In $Sn_2[SP(S)(OC_6H_5)_2]_4$, the dithiophosphate groups are anisobidentate and the two tin atoms are held together by tri-coordinated sulfur atoms and $\eta^6\text{-}C_6H_5$ interactions with the tin lone pairs.[111] In the crystal structure of $Ag_4[SC(S)N(C_3H_7\text{-}n)_2]_4$, the silver atoms form a distorted octahedron with six relatively short and six relatively long edges.[112] The long edges form two triangles related by an inversion center. Of each dithiocarbamate ligand, one sulfur is linked to two silver atoms, while the other is only linked to one. In $Zn_2[SC(S)N(CH_3)_2]_4$, two ligands are bidentate and the other two bridge two zinc atoms,[113] whereas, in the corresponding diethyldithiocarbamate analogue,[18,114] which is monomeric, both ligands are bidentate and the zinc atom is penta-coordinated.

Structural aspects of organogermanium chemistry is no less interesting.[115] In $(\eta^1\text{-}C_5H_5)GeH_3$[116] and $(C_6H_5)_4Ge$[117,118] the geometry around germanium is tetrahedral, which is common. However, in bis(3,3-dimethyl-1-butyneyl)hemiporphyrazine germanium,[119] the geometry around the metal is octahedral, whereas, in $GeCl_4.N(CH_3)_3$ it is trigonal bipyramidal.[70] A square planar geometry for germanium is observed in the structure of

$[(C_4H_4O_2)_2GeCl][N(C_2H_5)_4]$.[119]

To fully illustrate the nature of the dithiocarbamate and dithiophosphate groups, their effect on organogermanium moieties, and to confirm the implied spectroscopic results, crystal structures of chloromethyl(*N*,*N*'-dimethyldithiocarbamato)germane (2), dimethylbis(*N*,*N*'-dimethyldithiocarbamato)germane (3), dichloromethyl(*N*,*N*'-dimethyldithiocarbamato)germane (4), triphenyl-(*O*,*O*'-dimethyldithiophosphato)germane (17), diphenylbis(*O*,*O*'-dimethyldithiophosphato)germane (18) and phenyltris(*O*,*O*'-dimethyldithiophosphato)germane (19) were determined.

VIII.1 Crystallographic Measurements

Suitable crystals with well defined faces were selected for data collection. The crystal was sealed in a Lindemann capillary tube and mounted along the largest dimension on the four-circle automated diffractometer under the control of a Nova 1200 computer. The diffractometer, at a take-off angle of 6.1°, was equipped with a molybdenum X-ray tube and a highly oriented graphite monochromator (λ = 0.71069 Å, $2\theta_m$ = 12.2°) and operated at 50 kV and 20 mA.

The crystal was optically centered in a random orientation. Determination of preliminary cell parameters and the orientation matrix were carried out as described in the *Syntex P2₁ Operations Manual*. Examination of the ω scans of several low angle centered reflections showed no defects in the crystals except in compound 4; the full peak width at half height was always less than 0.2°.

The axial photographs were taken about each of the three chosen axes of the cell to determine 2 symmetry and consequently the crystal system and to determine the true lengths of the axial vectors and discard their submultiples. A unique set of data in the shell defined by $15° < 2\theta < 30°$ was collected next at a fast scan rate ($19.88°min^{-1}$). A set of 15 strong reflections, widely separated in reciprocal space, was chosen from these data and formed the basis for the determination of accurate cell parameters and the orientation matrix.

Intensity data were collected via a θ(crystal)-2θ(counter) scan in 96 steps using bisecting geometry. The scan was from $[2\theta(MoK\alpha_1(0.70926\ \text{Å}))-1.0°]$ to $[2\theta(MoK\alpha_2(0.71354\ \text{Å}))+1.0°]$. Backgrounds were measured both at the beginning and at the end of the scan, each for 25% of the time of the scan. The stability of the system and the crystal was monitored by measuring three strong check reflections after every 50 or 60 data. Whenever the intensities of these reflections decreased during the course of data collection an appropriate scaling factor was applied. During data collection, if any of the scan step exceeded 5000 counts, it was subjected to a linear correction for coincidence losses. Such reflections had greater magnitudes of intensity and were remeasured, along with the three monitor reflections at 35 kV and 15 mA.

Data were corrected for Lorentz and polarization effects. The Lp factor[121] for a monochromator in the equatorial mode is given by the following equation, which assumes that the graphite

monochromator crystal is 50% mosaic and 50% perfect:

$$L_p = \frac{0.5}{\sin 2\theta}\left[\left(\frac{1+(\cos^2 2\theta_m)(\cos^2 2\theta)}{1+\cos^2 2\theta_m}\right)\cdot\left(\frac{1+|\cos 2\theta_m|\cos^2 2\theta}{1+\cos 2\theta_m}\right)\right]$$

The monochromator angle, $2\theta_m$ is 12.2° for MoKα radiation. An analytical absorption correction was always applied to the data. Details of the crystal and intensity data collection for all of the compounds are provided in Tables 36 to 38.

VIII.2 Structure Determination and Refinement

1. $(CH_3)_2Ge[SC(S)N(CH_3)_2]Cl$ (2)

The data contained systematic absences $h0l$ ($h = 2n+1$) and $0k0$ ($k = 2n+1$), consistent with the space group $P2_1/c$ (C_{2h}^5, No. 14). The position of the germanium atom was determined by a sharpened Patterson synthesis, and subsequent difference maps revealed the remaining atoms. Complete anisotropic refinement minimizing the function $\Sigma w(|F_o|-|F_c|)^2$ converged at $R = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.0319$ and $R_w = [\Sigma w\Delta^2/wF_o^2]^{1/2} = 0.0382$, based on 90 variables and 1299 unique reflections. Hydrogen atoms of the methyl groups were included at the idealized positions (C-H = 0.95 Å, H-C-H = 109.5°) with isotropic thermal parameters set at 0.1 Å^2 greater than that of the corresponding carbon atom. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$ with a weighting scheme of the form $w = 1/[\sigma(F)+\rho F^2]$ to give the final ρ value of 0.005. Final fractional coordinates and thermal parameters are listed in Table 39. Bond distances and angles are

given in Table 40.

2. $(CH_3)_2Ge[SC(S)N(CH_3)_2]_2$ (3)

An analysis of systematic absences (hkl, $h+k$, $k+l$, $l+h$ = $2n$; $0kl$, $k+l$ = $4n$; $h0l$, $l+h$ = $4n$; $hk0$, h, k, = $2n$; $h00$, h = $4n$; $0k0$, k = $4n$; $00l$, l = $4n$) indicated that the space group was $Fdd2$ (C_{2v}^{19}, No. 43). The structure was solved by a sharpened Patterson synthesis and refined by a full-matrix least-squares method to R = 0.0283 and R_w = 0.0295 from 135 variables and 1107 unique reflections. The methyl hydrogens were refined as rigid groups. A weighting scheme of $w = 1/[\sigma(F)+\rho F^2]$ was employed with a final ρ value of 0.0001. In the last cycle no parameter changed by more than 2.2σ. Final fractional coordinates and thermal parameters are listed in Table 41. Bond distances and angles are given in Table 42.

3. $CH_3Ge[SC(S)N(CH_3)_2]Cl_2$ (4)

A crystal of suitable dimensions was sealed in a capillary tube and was mounted on the diffractometer. The crystal decayed rapidly during data collection and the sublimed powder adhered to the capillary tube around it, causing a signigicant loss in intensities. For this reason various sets of data were collected using different crystals at faster variable scan speeds of 4.88 - 9.77°min^{-1}. Despite this, even for the best crystal, data collection had to be terminated at $2\theta_{max}$ = 30°, when the intensities of the three monitor reflections dropped by 70%. The other difficulty encountered was that of twinning. Nevertheless, from 15 high angle reflections, the unit cell a = 19.373(9),

b = 6.478(2), c = 34.889(2) Å; β = 99.94(3)° with Z = 8, was obtained. The systematic absences ($0k0$, $k = 2n+1$; $h0l$, $h = 2n+1$, $l = 2n+1$), indicated the possible space group $P2_1/c$ and the reflection twinning of the crystal on 001.[122] Since the fit of the two mirrored lattices was close to ideal, the data was reduced with the c axis halved using the transformation matrix (0 0 1/2 0 −1 0 1 0 0). All the reflections with non-integral values of l were rejected. This data was clearly erroneous and incomplete. Yet, this approximation allowed for the location of the non-hydrogen atoms but the structure could only be refined to R = 0.19.

4. $(C_6H_5)_3Ge[SP(S)(OCH_3)_2]$ (17)

The space group $P\bar{1}$ was used and later assumed correct because of successful refinement of the structure. The position of the germanium atom was determined by a Patterson synthesis and the remaining atoms were revealed by subsequent difference maps. Complete anisotropic refinement minimizing the $\Sigma w(|F_o|-|F_c|)^2$ function converged at R = 0.0325 and R_w = 0.0353. Hydrogen atoms were included at idealized positions with isotropic U's set at 0.1 Å^2 greater than that of the corresponding carbon atom. A weighting scheme of the form $w = 1/[\sigma^2(F)+pF^2]$ with a final p value of 0.0001 was employed. Final fractional coordinates and thermal parameters are listed in Table 43. Bond distances and angles are given in Table 44.

5. $(C_6H_5)_2Ge[SP(S)(OCH_3)_2]_2$ (18)

The space group $P\bar{1}$ was assigned and subsequently confirmed

by structure solution. The structure was solved by a Patterson synthesis and refined by a full-matrix least-squares method to R = 0.0581 and R_w = 0.0628. Hydrogen atoms were placed at idealized positions and the weighting scheme included a final p value of 0.0001. A few peaks of the order of 1.2 $e\text{Å}^{-3}$ were found in the final difference map around the methoxy groups, suggesting some disorder. However, in the last cycle no parameter changed more than 0.1σ. Final fractional coordinates and thermal parameters are listed in Table 45. Bond distances and angles are given in Table 46.

6. $C_4H_8Ge[SP(S)(OCH_3)_2]_2$ (19)

Analysis of the systematic absences ($0kl$, $k+l$ = 2n+1; $hk0$, h = 2n+1) indicated that the space group was either $Pnma$ (D_{2h}^{16}, No. 62) or $Pn2_1a$ (standard setting $Pna2_1$(C_{2v}^9, No. 33)). The structure was solved by using the conventional heavy atom techniques in the centric space group $Pnma$. The position of the germanium atom was determined from a Patterson synthesis, and since there are four molecules in the unit cell, was placed at a special position x, 1/4, z with m symmetry. Subsequent Fourier maps revealed the positions of the remaining atoms. Since Z = 4, the phenyl ring and a dithiophosphate group were expected to lie on the mirror plane. However, the difference Fourier maps revealed that the P(2) atom was disordered across the mirror plane with a small separation (0.93 Å), and S(4) was disordered on the mirror plane. Some carbon atoms belonging to the methoxy and phenyl groups also showed evidence of positional disorder.

Consequently, S(4), P(2), O(3), C(1), C(2) and C(3) were refined isotropically with 50, 50, 100, 60, 60 and 50% occupancies respectively, and the rest of the atoms were refined anisotropically. The full-matrix least-squares refinement thus converged to $R = 0.0977$. Subsequent refinement in the space group $Pn2_1a$ resulted in no improvement. Hydrogen atoms were not included in the calculations. Unit weights were used throughout and in the final two cycles of refinement the largest shift/error ratio was 0.4, and the final difference map had a few peaks with intensities up to 1.6 $e\text{Å}^{-3}$ which were unconnected to the molecule and were without any chemical significance. Final fractional coordinates and thermal parameters are listed in Table 47. Anisotropic thermal parameters are shown in Table 48. Bond distances and angles are given in Table 49.

Scattering factors for all non-hydrogen atoms, including anomalous dispersion corrections for germanium, sulfur and phosphorus were obtained from Ibers and Hamilton,[123] and for hydrogen atoms from Stewart, Davidson and Simpson.[124] All calculations were performed on the IBM 3031 computer at the University of Windsor. Programs used during the structural analysis include local versions of *CHECK* (check reflections by P. W. R. Corfield), *PROC* (data reduction by W. Schmonsees), *SHELX* (Fourier synthesis and structure refinement by G. M. Sheldrick), *XANADU* (crystallographic calculations by P. Roberts and G. M. Sheldrick), *ORTEP* (thermal ellipsoid plotting program by C. K. Johnson) and *ABSORB* (analytical absorption correction by

D. Templeton and L. Templeton).

VIII.3 Structures of Dithiocarbamatogermanes.

Compounds 2 and 4 crystallize in the $P2_1/c$ and compound 3 in the $Fdd2$ space groups. The asymmetric units and ORTEP diagrams of 2 and 3 are shown in Figures 44 and 45. The germanium atom in compound 2 is essentially at the center of a distorted trigonal bipyramid, with the two carbon atoms of the methyl groups and one of the sulfur atoms occupying the equatorial positions. The chlorine atom clearly occupies one axial position while the second sulfur atom of the dithiocarbamate group occupies the second axial site but at a distance much greater than expected for a normal covalent Ge-S bond while forming an angle of 159.2(1)° rather than 180° with the Ge-Cl bond.

The Ge-C bond lengths (1.929(2), 1.925(2) Å) are typical of all methylgermanes and are remarkably close to those found in $(CH_3)_2GeCl_2$ (1.928(6) Å from electron diffraction.[125] The Ge-S bond in the equatorial plane is of a length (2.254(1) Å) expected from the sum of the covalent radii of germanium and sulfur (2.25 Å),[5] and is similar to those in $(C_6H_5)_3GeS(C_6H_4\text{-}t)$ (2.229 Å)[126] and $[(CH_3)_3Ge]_2SW(CO)_5$ (average 2.275 Å).[127] By contrast, the Ge-Cl bond (2.251(1) Å) is appreciably longer than it is in $(CH_3)_2GeCl_2$ (2.143(4) Å)[125] but remarkably close to the length of the axial Ge-Cl bond in $GeCl_4.N(CH_3)_3$ (2.24(1) Å).[70] The assignment of ν(Ge-Cl) to 321 cm^{-1} is therefore reasonable and

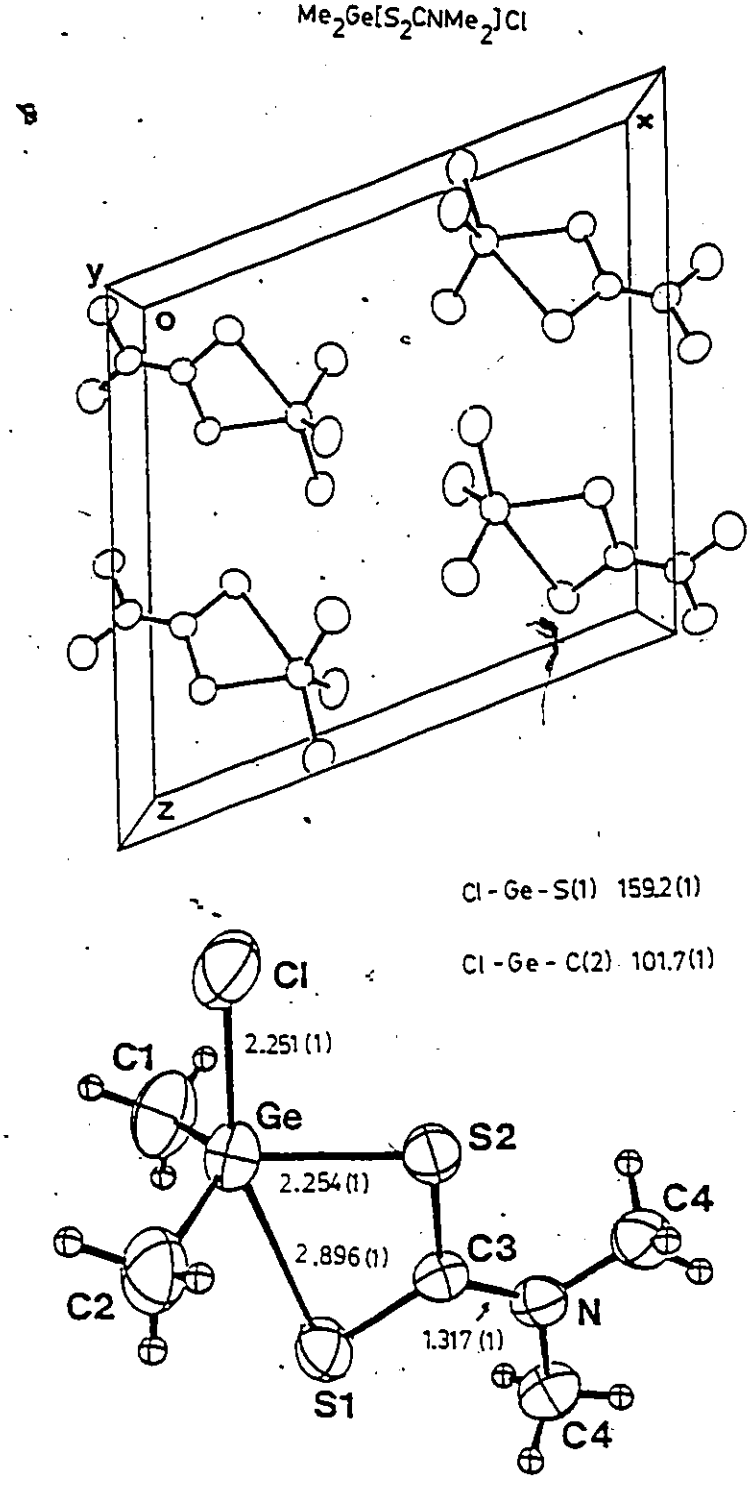
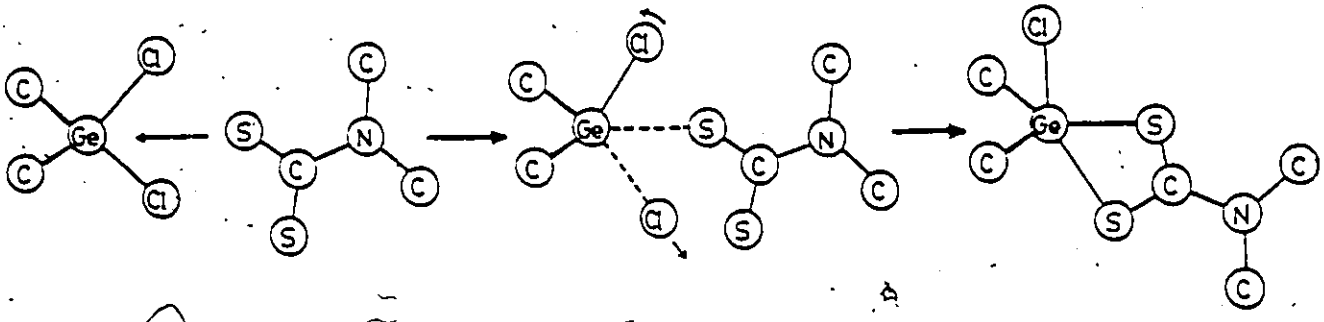


Figure 44 The Unit Cell and ORTEP Diagrams of $(CH_3)_2Ge[S_2CN(CH_3)_2]Cl$ (2).

consistent with the presence of a weaker Ge–Cl bond. Furthermore, the Ge–S distance (2.896(1) Å) for the second sulfur atom is so long that a second peak in the ν(Ge–S) stretching region cannot be expected.

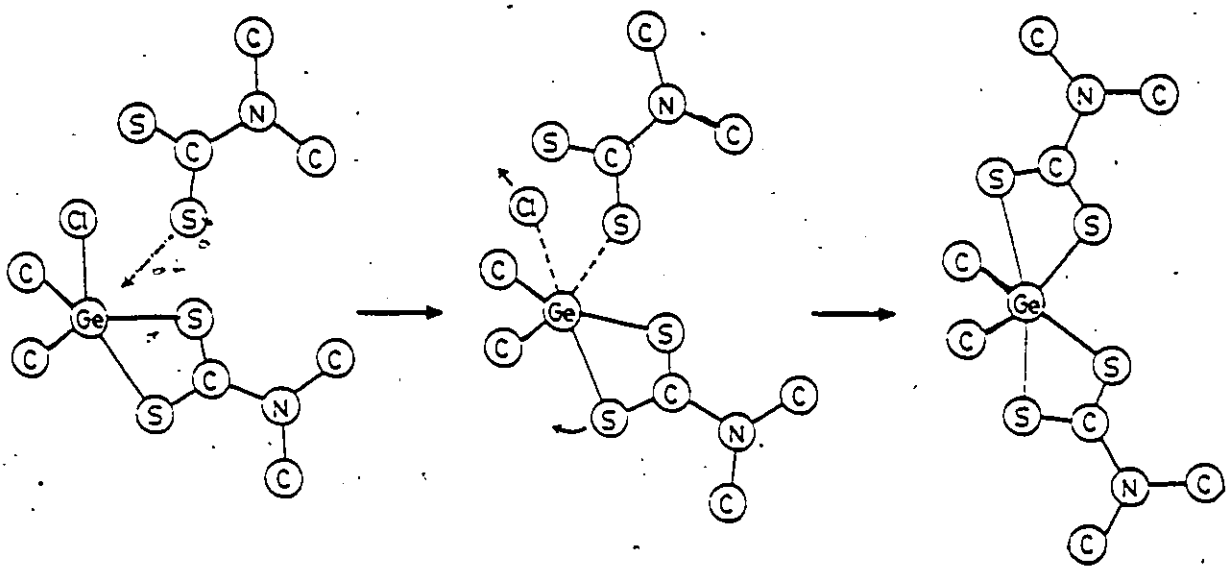
The C–Ge–C angle is hardly changed (121(4)° to 121.9(1)°) when one of the chlorine atoms in $(CH_3)_2GeCl_2$ is substituted by the dithiocarbamate group. If the reaction originates by a nucleophilic attact by a sulfur atom along the C_2 axis bisecting the Cl–Ge–Cl angle in $(CH_3)_2GeCl_2$, then this equatorial sulfur atom virtually remains at its attacking position, the CH_3 groups are unaffected, the remaining Cl atom is bent back to the axial position of a trigonal bipyramid, and the vacant site is partly occupied by the second sulfur atom. Presumably, with a monodentate attachment, the sulfur and chlorine atoms would simply rearrange to a pseudo-tetrahedral arrangement. However, the molecule is apparently "frozen" in this intermediate structure to give anisobidentate coordination.



The structure is similar to that of $(CH_3)_2Sn[SC(S)-N(CH_3)_2]Cl$,[128] although the C–Sn–C angle is considerably larger (128(2)°) and the axial Cl–Sn–S angle smaller (154.5(4)°) than

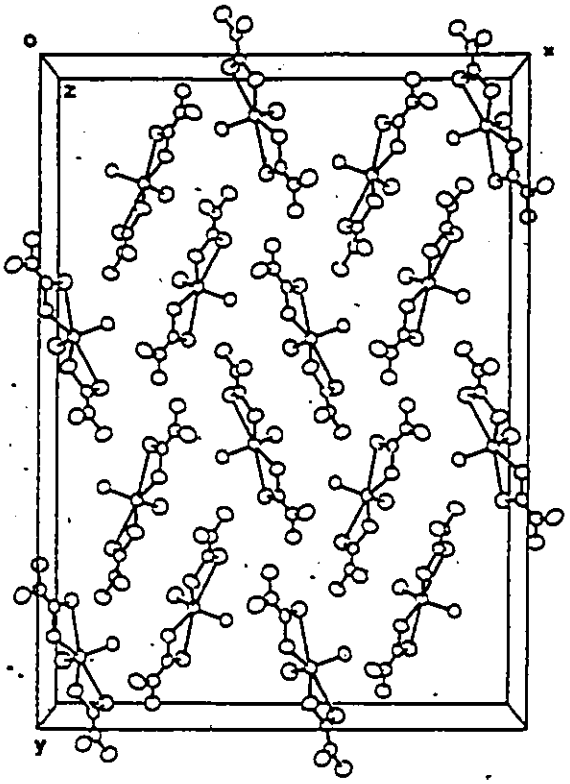
the corresponding angles in the germanium analogue. Both distortions seem surprising because a closer adherence to 120° and 180° angles might be anticipated on the larger tin atom.

The structure of compound 3 results from replacement of the chlorine atom of compound 2. In fact, the formation of the compound is an extension of the model involving the sequential replacement of both chloride atoms of $(CH_3)_2GeCl_2$ by dithiocarbamate groups. Replacement of the chlorine atom in compound 2 could result from attack between the chlorine atom and the attached sulfur, so that the newly attached sulfur atom takes up a position that is *cis* to the existing strongly bonded sulfur atom which will be forced to move in the plane away from the incoming atom.



The new Ge–S bond is then formed in a pseudo-tetrahedral position relative to the Ge–C bonds with the existing Ge–S bond rotating to the other pseudo-tetrahedral position. The long Ge–S

$Me_2Ge[S_2CNMe_2]_2$



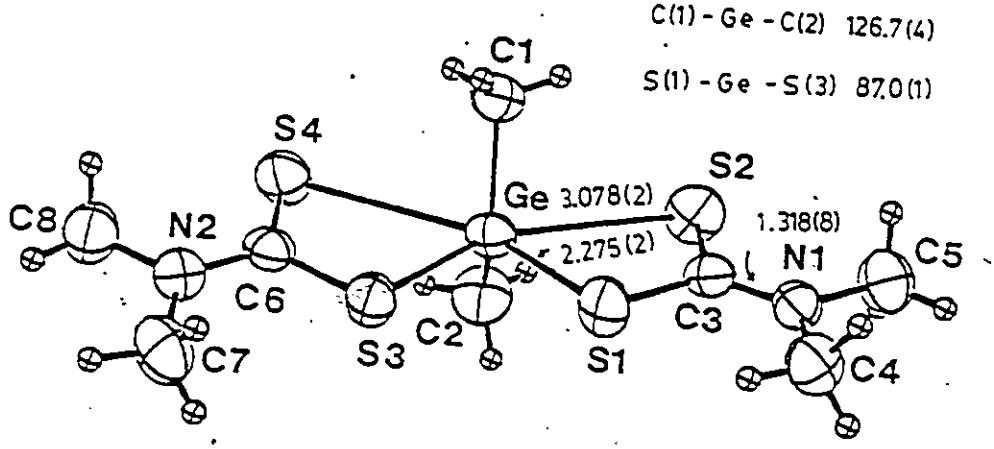


Figure 45 The Unit Cell and ORTEP Diagrams of $(CH_3)_2Ge[S_2CN(CH_3)_2]_2$ (3).

bond also rotates and the new one forms in the open position to make an apparent hexa-coordinated structure.

There are striking similarities between the Ge-C bond distances and the C-Ge-C angles of compound 3 and $(CH_3)_2GeBr_2$,[12] consistent with the observation from nmr spectroscopy that the effect of the dithiocarbamate group was similar to that of a bromine atom. Thus, the average Ge-C bond length in compound 3 is 1.915(7) Å compared to 1.911(12) Å in $(CH_3)_2GeBr_2$, and their C-Ge-C angles are 126.7(4)° and 124(7)° respectively. These values are remarkably close given the difference in the phases. Because four sulfur atoms are accommodated in a plane, it is not surprising that the S-Ge-S angle (87.0(1)°) is smaller than the Br-Ge-Br angle (104(2)°).

The dithiocarbamate ligand shows very similar features in both compounds 2 and 3. The S-Ge--S angle is 68.5(1)° in 2 closing down to 65.2(1)° and 64.0(1)° in the more crowded bis compound. The Ge-S bonds are longer in the more crowded compound 3 (average 2.278(2) and 3.118(2) Å respectively). The two C=S bonds in compound 2 (1.690(2) and 1.750(2) Å) are comparable with the average values of compound 3 (1.659(8) and 1.758(8) Å). The same applies to the C=N and C-N bond distances in compounds 2 (1.317(2) and average 1.458(3) Å respectively) and 3 (average 1.318(10) and average 1.443(10) Å respectively). The short C-N distance is in accordance with infrared spectroscopic evidence.

Compound 3 may be alternatively described as pseudo-tetrahedral, rather than as pseudo-octahedral. If the germanium

atom were in an octahedral environment the methyl groups would be required to be in *trans* positions, thereby making the C-Ge-C skeleton linear. However, the C-Ge-C angle in compound 3 is only 126.7(4)°, which is much closer to the tetrahedral angle than 180°. The analogous tin compound[130] has a similar structure, but with a C-Sn-C angle of 136(1)°. The tetrahedral description is consistent with the similarities of the ν(Ge-C) stretches and the Ge-CH_3 chemical shifts of $(CH_3)_2GeBr_2$ and compound 3.

Because of the twinning and decay problems the structure of compound 4 could not be completely refined. However, the structure is similar to compound 2 with a strongly held sulfur atom, the methyl group and one chlorine atom occupying the planar positions of a pseudo-trigonal bipyramid and the second chlorine atom and the weakly held sulfur atom occupying the axial positions.

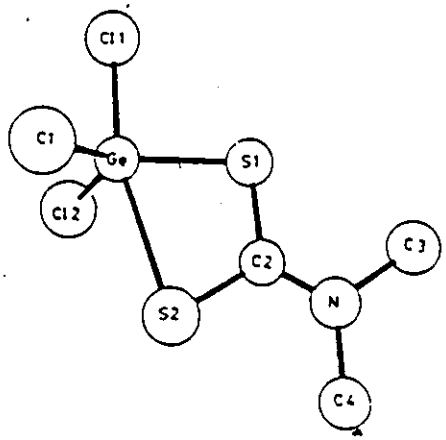


Figure 46 The ORTEP Diagram of $CH_3Ge[S_2CN(CH_3)_2]Cl_2$ (4).

VIII.4 Structures of Dithiophosphatogermanes.

Compounds 17 and 18 crystallize in $P\bar{1}$ symmetry and compound 19 in the *Pnma* space group. The unit cells and the ORTEP diagrams of the compounds are illustrated in Figures 47 to 49. The dithiophosphate groups are clearly monodentate with the terminal non-bonded sulfur atom twisted as far away as possible from the germanium atom. The molecules of compound 19 have crystallographically dictated m symmetry. The mirror plane passes through the germanium atom, one of the dithiophosphate groups and the phenyl ring. This is not unexpected in terms of symmetry, the GeS_3 unit being basically C_{3v}. However, this is rather unusual in view of the bulkiness of the dithiophosphate groups. The structure of 17 is notably similar to that of its tin analogue, $(C_6H_5)_3Sn[SP(S)(OC_2H_5)_2]$,[131] which is described as one of a kind among organotin dithiophosphates. On the other hand, the tin analogue for compound 18, $(C_6H_5)_2Sn[SP(S)-(OC_3H_7\text{-}i)_2]_2$[132] has fully bidentate dithiophosphate groups with the tin atom in an octahedral environment with the C-Sn-C angle opening up to 180°. Thus, this structure is strikingly different from that of compound 18.

The geometry around the germanium atom in compounds 17, 18 and 19 is that of a distorted tetrahedron. The spatial requirements of the phenyl groups appear to be greater than those of the dithiophosphate groups, since the C-Ge-C angle in compound 18 (115.8(3)°) is appreciably larger than the S-Ge-S angle (103.4(1)°). In compound 17 the average value of the three

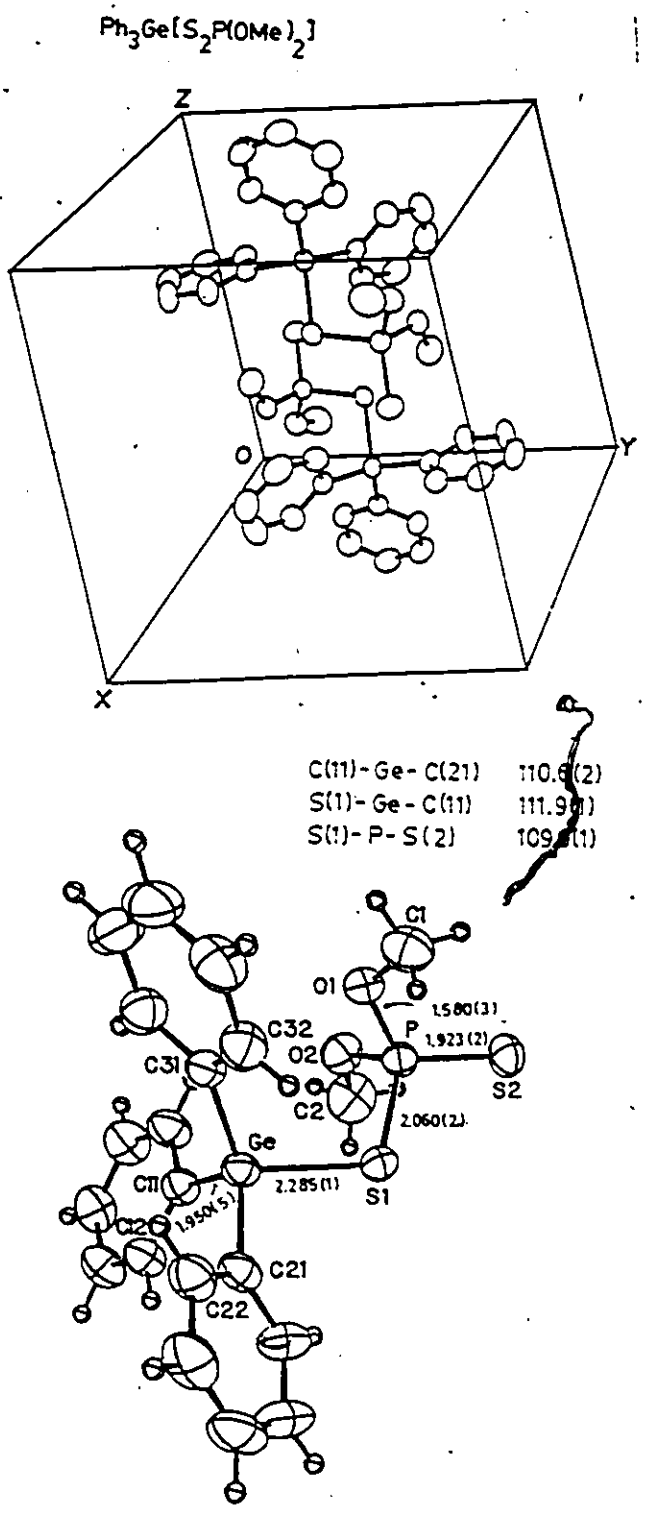
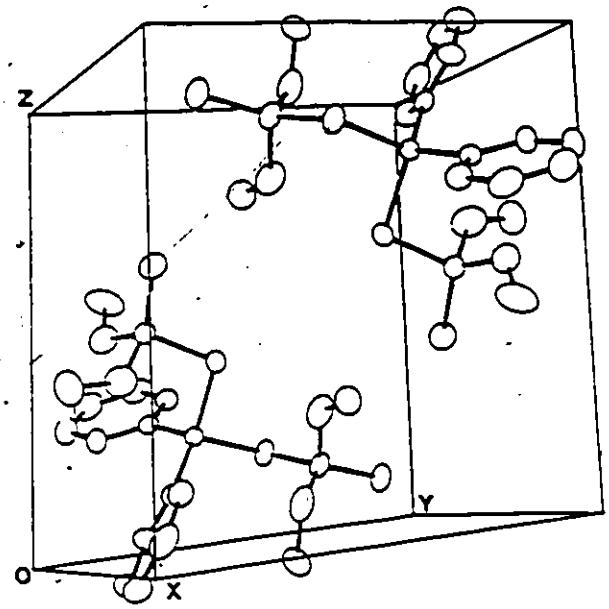


Figure 47 The Unit Cell and ORTEP Diagrams of $(C_6H_5)_3Ge[S_2P(OCH_3)_2]$ (17).

C-Ge-C angles is 112.3° while that of the three C-Ge-S angles is 106.3°. In compound 19 the three S-Ge-S angles (average 102.4(3)°) are considerably shorter than the three C-Ge-S angles (average 111.0(3)°). This observation is consistent with Bent's rule.[133] The more electronegative sulfur atoms clearly favor orbitals with more p character and angles are closer to 90°. The C-Ge-S angles in compound 17 vary considerably from 98.7(1)° to 111.9(1)°. The smallest angle corresponds to the side of the teterahedron away from the methoxy groups of the dithiophosphate ligand, where there is least steric hindrance. However, the C-Ge-C angles correspond well with those observed in $(C_6H_5)_3$-GeBr.[134] It appears that the dithiophosphate group approaches along the apparent C_2 axis of $(C_6H_5)_3$GeCl between the carbon and chlorine atoms replacing the chlorine atom by one of the sulfur atoms. In this process, the second sulfur atom should be bound more strongly to phosphorus, or in other words, the P=S double bond is regenerated. The presence of this electron rich P=S bond in proximity of the phenyl groups on germanium results in the bond being rotated by 180° along the bridging P-S bond from its original attacking position. In addition to the presence of phenyl groups, the small van der Waals radius of the germanium atom may be a contributing factor in determing the nature of bonding of the dithiophosphate groups. The formation of compounds 18 and 19 may be viewed as the simultaneous attack of dithiophosphate anions to replace the chlorine atoms and subsequent repetition of the process.

$Ph_2Ge[S_2P(OMe)_2]_2$



C(11) - Ge - C(21)	115.8(3)
S(1) - Ge - S(3)	103.4(1)
S(1) - P(1) - S(2)	111.9(1)
S(3) - P(2) - S(4)	112.4(1)

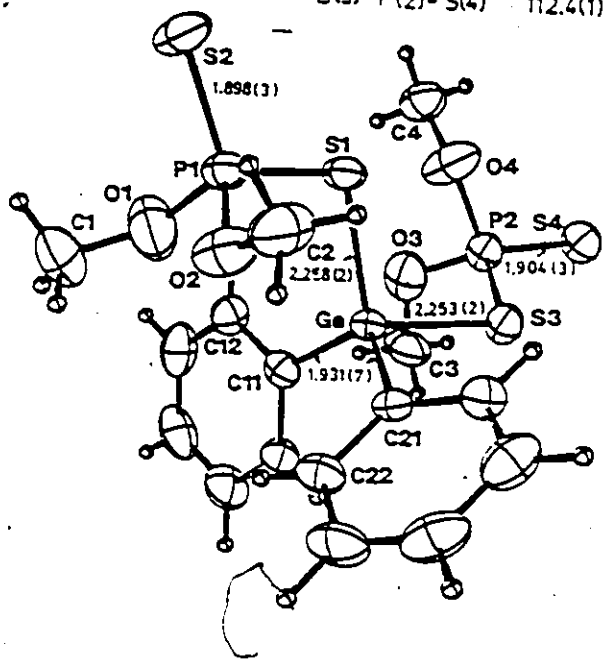


Figure 48 The Unit Cell and ORTEP Diagrams of $(C_6H_5)_2Ge[S_2P(OCH_3)_2]_2$ (18).

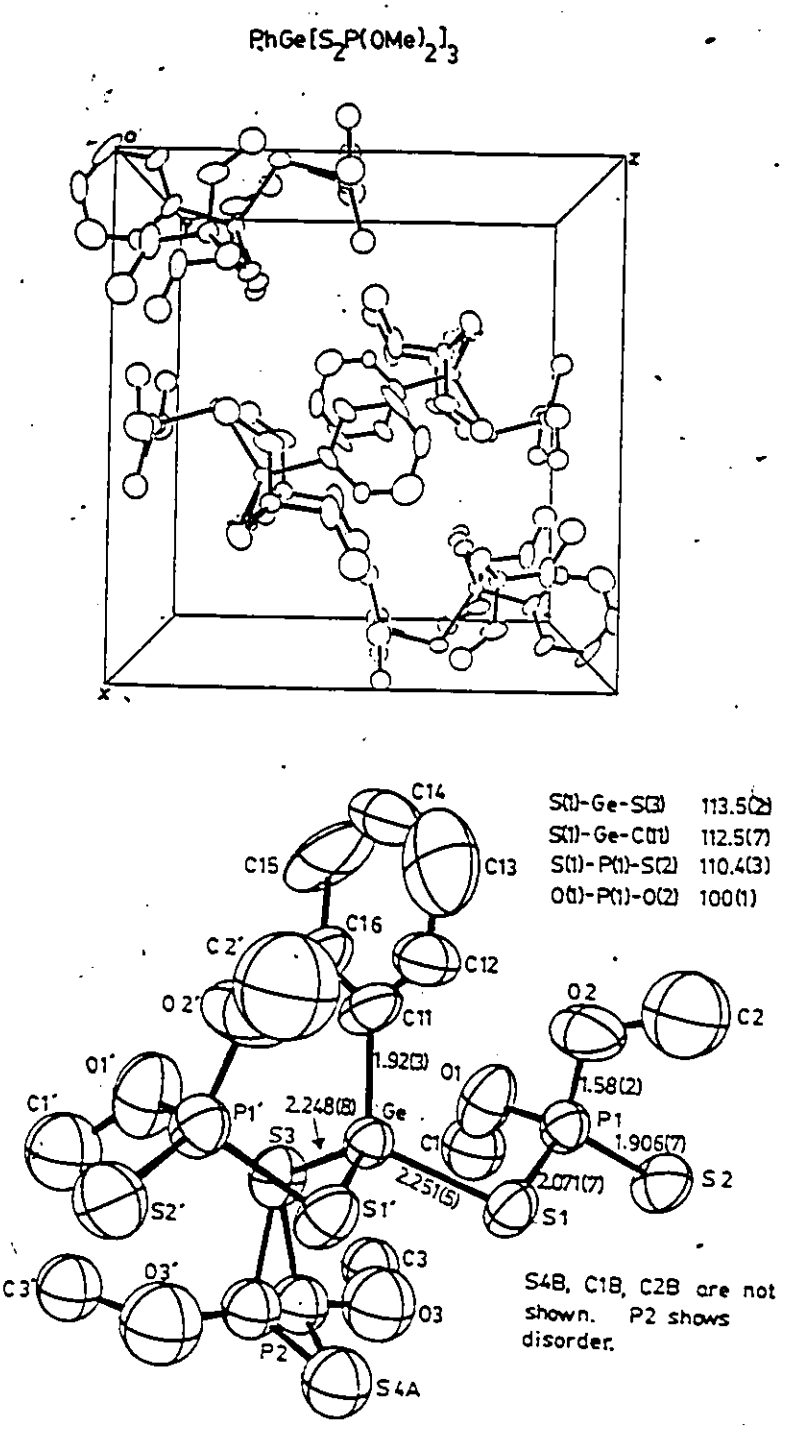
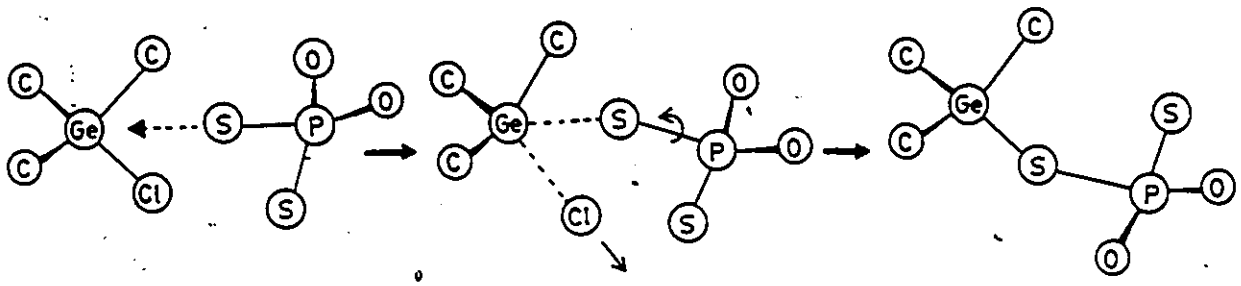


Figure 49 The Unit Cell and ORTEP Diagrams of $C_6H_5Ge[S_2P(OCH_3)_2]_3$ (19).



The Ge–S bond lengths in these compounds are comparable to chlorodimethyl(*N*,*N*'–dimethyldithiocarbamato)germane (2) and dimethylbis(*N*,*N*'–dimethyldithiocarbamato)germane (3). The average bond lengths in compounds 18 and 19 are shorter than in 17. The Ge–S bond lengths in compound 18 are 2.257(2) and 2.253(2) Å, in 19 are 2.251(5), 2.248(8) and 2.251(5) Å, while in 17 the bond length is 2.285(1) Å. Similarly, the average Ge–C bond length in 18 is 1.931(7), in 19 is 1.92(3) Å, whereas in 17 it is 1.941(5) Å. This slight shortening of all Ge–C and Ge–S bonds, as the more electronegative dithiophosphate group replaces a phenyl group, is to be expected and is also noticeable for the average Ge–C bond length in $(C_6H_5)_4Ge$ (1.957(4) Å),[117,118] shortening to 1.935(10) Å in $(C_6H_5)_3GeBr$[134] or 1.942(3) Å in $[(C_6H_5)_3Ge]_2O$.[135] As with the C–Ge–S bond angles, the Ge–C bond lengths show more variation in compound 17 than in 18. Such distortions of bond angles and bond distances are more evident in the dithiophosphate groups of compounds 18 and 19 than in compound 17. Within the distorted tetrahedron around phosphorus, the angles spanned by

oxygen atoms are, as expected, smaller than those spanned by sulfur atoms. Thus, the O-P-O angle in compound 17 is 95.7(2)° compared to the S-P-S angle of 109.1(1)°. The average O-P-O angle in 18 is 97.7(5)°, which is considerably smaller than the average S-P-S angle 112.2(1)°. A similar trend also continues in compound 19, the average O-P-O and S-P-S angles being 100(1)° and 112.7(5)° respectively. The effect of crowding in compounds 18 and 19 are reflected in the considerable distortion and dissimilarity of their dithiophosphate groups. For example, in 17 the P-O-C angles are 120.2(3) and 121.2(4)° with the P-O bond lengths being 1.580(3) and 1.578(3) Å. In 18 the dithiophosphate group containing P(1) has P-O-C angles of 127.4(8) and 119.1(6)°, and P-O bond lengths of 1.609(8) and 1.520(6) Å, while the group containing P(2) has P-O-C angles that are 125.2(7) and 118.4(7)° with P-O bond lengths of 1.614(7) and 1.530(7) Å. The O-C distances in 18 containing P(1) are 1.319(11) and 1.455(10) Å, while those containing P(2) are 1.475(10) and 1.330(10) Å. In both dithiophosphate groups of 18, the longer P-O distances are associated with shorter O-C distances. These distortions, which appear to be centered around P-O-C rather than S-P-S links, have not been observed in similar tin and lead compounds.

The terminal P=S bonds are shorter than the bridging P-S bonds. In compound 17 the bond lengths are 1.923(2) and 2.060(2) Å and in 18 1.898(3) and 2.043(3) Å for P(1) and 1.904(3) and 2.045(3) Å for P(2). The P=S distances are comparable to those found in non-metal systems exemplified by $[SP(S)(OC_3H_7\text{-}i)_2]_2$

(1.908(3) Å)[136] and $\overline{SCH_2CH_2SP(S)Cl}$ (1.910(5) Å).[137] In metal dithiophosphates, irrespective of their mode of bonding, the P-S distances only undergo relatively small changes. In general, however, the P=S bonds are usually longer than observed in these compounds as exemplified by those found in $V[SP(S)(OC_2H_5)_2]_3$ (average 1.971(9) Å)[138] or $Ni[SP(S)(OC_2H_5)_2]_2$ (average 1.97(2) Å).[139] Even in the tin analogue of 17, $(C_6H_5)_3Sn[SP(S)(OC_2H_5)_2]$,[131] the P=S distance is 1.931(1) Å. Apparently, the shortest P=S bond reported previously is in $Te[SP(S)(OCH_3)_2]_2$ (1.923(7) Å),[140] which also has monodentate ligands.

The contrast between the structure of compound 18 and that of the similar tin compound is particularly surprising in view of the similarity between the structure of 17 and that of $(C_6H_5)_3Sn[SP(S)(OC_2H_5)_2]$. The structure of $(C_6H_5)_2Sn[SP(S)(OC_3H_7\text{-}i)_2]_2$ consists of octahedrally coordinated tin with the phenyl groups *trans* to one another and with symmetrically chelating dithiophosphate ligands. The tin atoms are related by a unit translation along the *c* axis (6.341(8) Å), thereby making the structure a virtual polymer. This is in total contrast to the structure of 18, in which, as in 17, the P=S bonds are located well away from the germanium atom and indeed are well away from adjacent molecules. The shortest Ge--S intermolecular distance in 17 is 5.253(1) Å and in 18 is 5.363(2) Å, both of which are considerably greater than the sum of the van der Waals radii of 3.85 Å. This isolation of the P=S bond may account for the fact that it is relatively short and thus is not able to coordinate

effectively. There is clearly no indication of even the anisobidentate behaviour found for the sulfur ligand in the germanium dithiocarbamates.

Table 36 Crystallographic Data for $(CH_3)_2Ge[S_2CN(CH_3)_2]Cl$ (2) and $(CH_3)_2Ge[S_2CN(CH_3)_2]_2$ (3)

	Compound 2	Compound 3
a (Å)	12.682(4)	25.045(3)
b (Å)	7.532(3)	34.740(3)
c (Å)	12.085(4)	6.896(6)
β, (°)	109.88(2)	
V (Å^3)	1085(1)	6000(10)
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c$	$Fdd2$
mol wt	258.3	343.1
Z	4	16
ρ_{calcd} (gcm^{-3})	1.58	1.52
ρ_{obsd} (gcm^{-3})	1.56	1.53
cryst dimens (mm)	0.08 x 0.23 x 0.30	0.12 x 0.27 x 0.38
radiation	Mo K_α 0.71069 Å	Mo K_α 0.71069 Å
monochromator	highly oriented graphite	highly oriented graphite
temp (°C)	21	21
abs coeff(μ, cm^{-1})	32.71	24.71
min abs corr	1.589	1.31
max abs corr	3.721	1.57
2θ angle (°)	4 to 50	4 to 50

Table 36 continued

	Compound 2	Compound 3
scan type	coupled	coupled
	θ(cryst)/2θ(counter)	θ(cryst)/2θ(counter)
scan width	$K\alpha_1$ − 1° to $K\alpha_2$ + 1°	$K\alpha_1$ − 1° to $K\alpha_2$ + 1°
scan speed(°/min)	variable, 2.02 − 4.88	2 − 5
bkgd/scan time	0.5	0.5
total reflcns measd	2267 ($+h$, $+k$, $\pm l$)	1599 ($+h$, $+k$, $+l$)
unique data used	1299 [$I \geq 3\sigma(I)$]	1107 [$I \geq 3\sigma(I)$]
no. of param (NP)	91	136
R	0.0319	0.0283
R_w	0.0382	0.0295

Table 37 Crystallographic Data of $(C_6H_5)_2Se[S_2P(OCH_3)_2]$ (17) and $(C_6H_5)_2Se[S_2P(OCH_3)_2]_2$ (18)

	Compound 17	Compound 18
a (Å)	10.311(4)	9.813(9)
b (Å)	11.282	10.345(7)
c (Å)	11.517(4)	11.837(7)
α (°)	101.47(3)	89.04(5)
β (°)	113.68(3)	85.28(6)
γ (°)	110.31(3)	82.29(6)
V (Å^3)	1057.5(8)	1186.7(16)
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
mol wt	460.6	540.6
Z	2	2
ρ_{calcd} (gcm^{-1})	1.45	1.51
ρ_{obsd} (gcm^{-1})	1.42	1.52
cryst dimns (mm)	0.14 x 0.37 x 0.38	0.12 x 0.23 x 0.38
abs coeff(μ) cm^{-1}	16.53	17.07
min abs corr	1.225	1.214
max abs corr	1.898	1.666
total reflcns measd	3748 ($+h$, $\pm k$, $\pm l$)	4207 ($+h$, $\pm k$, $\pm l$)
unique data used	2738 [$I \geq 3\sigma(I)$]	2675 [$I \geq 3\sigma(I)$]
no. of params (NP)	235	244
R	0.0325	0.0581
R_w	0.0353	0.0628

Table 38 Crystallographic Data[a] of $C_4H_6Se[S_2P(OCH_3)_2]_2$ (19)

a (Å)	13.673(4)
b (Å)	14.566(3)
c (Å)	13.154(3)
V (Å^3)	2620(1)
cryst syst	orthorhombic
space group	*Pnma*
mol wt	621.2
Z	4
ρ_{calcd} (gcm^{-1})	1.57
ρ_{obsd} (gcm^{-1})	1.55
cryst dimns (mm)	0.25 x 0.28 x 0.43
abs coeff(μ, cm^{-1})	17.59
min abs corr	1.515
max abs corr	1.783
total reflcns measd	2765 ($+h$, $+k$, $+l$)
unique data used	1222
no. of param (NP)	128
R	0.0977
R_w	0.0977

[a] Data measured at 45 kV, 20 mA.

Table 39 Final Fractional Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms of $(CH_3)_2Ge[S_2CN(CH_3)_2]Cl$ (2) with Standard Deviations in Parentheses

	x	y	z	U_{eq}[a] ($Å^2 \times 10^3$)
Ge	0.3136(1)	0.09292(6)	0.34074(4)	51.5(3)
Cl	0.3503(1)	−0.0777(2)	0.5029(1)	73(1)
S(1)	0.1851(1)	0.2725(2)	0.1255(1)	58(1)
S(2)	0.1279(1)	0.0522(1)	0.2986(1)	47(1)
N	−0.0220(3)	0.1659(4)	0.1018(3)	30(2)
C(1)	0.3812(5)	−0.0470(8)	0.2486(5)	81(4)
C(2)	0.3741(4)	0.3177(7)	0.4073(5)	70(3)
C(3)	0.0857(3)	0.1661(5)	0.1644(3)	40(2)
C(4)	−0.0645(4)	0.2563(6)	−0.0119(3)	52(2)
C(5)	−0.1058(4)	0.0765(6)	0.1391(5)	56(2)

[a] U_{eq} for the non-hydrogen atoms is calculated from the refined anisotropic thermal parameters. $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*a_ia_j$.

Table 40 Bond Distances and Angles of $(CH_3)_2Ge[S_2CN(CH_3)_2]Cl$ (2)

Distances (Å)

Ge–Cl	2.251(1)	S(1)–C(3)	1.690(2)
Ge–S(1)	2.896(1)	S(2)–C(3)	1.750(2)
Ge–S(2)	2.254(1)	N–C(3)	1.317(2)
Ge–C(1)	1.929(2)	N–C(4)	1.463(3)
Ge–C(2)	1.925(2)	N–C(5)	1.453(3)

Angles (°)

Cl–Ge–S(1)	159.2(1)	C(1)–Ge–C(2)	121.9(1)
Cl–Ge–S(2)	90.7(1)	Ge–S(1)–C(3)	76.9(1)
S(1)–Ge–S(2)	68.5(1)	Ge–S(2)–C(3)	96.4(1)
Cl–Ge–C(1)	101.2(1)	C(3)–N–C(4)	121.2(2)
S(1)–Ge–C(1)	87.8(1)	C(3)–N–C(5)	123.2(2)
S(2)–Ge–C(1)	115.6(1)	C(4)–N–C(5)	115.6(2)
Cl–Ge–C(2)	101.7(1)	S(1)–C(3)–N	124.5(1)
S(1)–Ge–C(2)	89.1(1)	S(2)–C(3)–N	117.6(1)
S(2)–Ge–C(2)	116.7(1)	S(1)–C(3)–S(2)	117.9(2)

Table 42 Bond Distances and Angles of $(CH_3)_2Ge[S_2CN(CH_3)_2]_2$ (3)

Distances (Å)

Ge–S(1)	2.275(2)	S(3)–C(6)	1.748(7)
Ge–S(2)	3.078(2)	S(4)–C(6)	1.661(8)
Ge–S(3)	2.281(2)	N(1)–C(3)	1.318(8)
Ge–S(4)	3.158(2)	N(1)–C(4)	1.440(10)
Ge–C(1)	1.910(6)	N(1)–C(5)	1.455(8)
Ge–C(2)	1.921(7)	N(2)–C(6)	1.318(8)
S(1)–C(3)	1.759(7)	N(2)–C(7)	1.439(10)
S(2)–C(3)	1.658(7)	N(2)–C(8)	1.439(9)

Angles (°)

S(1)–Ge–S(2)	65.2(1)	Ge–S(3)–C(6)	100.8(2)
S(1)–Ge–S(3)	87.0(1)	Ge–S(4)–C(6)	73.5(2)
S(2)–Ge–S(4)	144.0(1)	S(1)–C(3)–S(2)	120.1(4)
S(3)–Ge–S(4)	64.0(1)	S(1)–C(3)–N(1)	115.0(5)
S(1)–Ge–C(1)	107.4(3)	S(2)–C(3)–N(1)	124.9(5)
S(1)–Ge–C(2)	112.5(2)	S(3)–C(6)–S(4)	121.6(4)
S(2)–Ge–C(1)	84.2(2)	S(3)–C(6)–N(2)	115.4(6)
S(2)–Ge–C(2)	81.9(2)	S(4)–C(6)–N(2)	123.0(6)
S(3)–Ge–C(1)	109.1(2)	C(3)–N(1)–C(4)	125.1(6)
S(3)–Ge–C(2)	106.9(2)	C(3)–N(1)–C(5)	119.8(7)
S(4)–Ge–C(1)	80.4(2)	C(4)–N(1)–C(5)	115.1(6)
S(4)–Ge–C(2)	81.6(2)	C(6)–N(2)–C(7)	122.3(7)
C(1)–Ge–C(2)	126.7(4)	C(6)–N(2)–C(8)	121.0(7)
Ge–S(1)–C(3)	99.6(3)	C(7)–N(2)–C(8)	116.7(6)
Ge–S(2)–C(3)	75.1(2)		

Table 41. Final Fractional Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms of $(CH_3)_2Ge[S_2CN(CH_3)_2]_2$ (3)

	x	y	z	U_{eq} ($Å^2 \times 10^3$)
Ge	0.06076(3)	0.41714(2)	0.25000(0)	42.3(3)
S(1)	0.0584(1)	0.4624(0)	0.0121(3)	59(1)
S(2)	0.1146(1)	0.4940(1)	0.3547(3)	66(1)
S(3)	0.0103(1)	0.3794(0)	0.0505(3)	55(1)
S(4)	0.0364(1)	0.3331(1)	0.4010(3)	66(1)
N(1)	0.1003(2)	0.5311(1)	0.0239(10)	48(3)
N(2)	−0.0216(2)	0.3091(2)	0.1085(10)	54(4)
C(1)	0.1318(2)	0.3972(2)	0.2585(15)	62(4)
C(2)	0.0167(3)	0.4305(2)	0.4678(12)	73(5)
C(3)	0.0930(3)	0.4999(2)	0.1298(10)	46(4)
C(4)	0.0824(3)	0.5361(2)	−0.1728(11)	61(5)
C(5)	0.1290(3)	0.5637(2)	0.1056(14)	69(5)
C(6)	0.0064(2)	0.3372(2)	0.1873(11)	43(4)
C(7)	−0.0511(3)	0.3141(2)	−0.0688(14)	79(6)
C(8)	−0.0249(3)	0.2719(2)	0.1995(14)	74(6)

Table 43 Final Fractional Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms of $(C_6H_5)_3Ge[S_2P(OCH_3)_2]$ (17)

	x	y	z	U_{eq} (Å² x 10^3)
Ge	0.16862(4)	0.05388(4)	0.35761(4)	37.0(2)
S(1)	0.2754	0.0791(1)	0.2189(1)	45(1)
S(2)	0.4406(1)	0.2991(1)	0.1122(1)	54(1)
P	0.3599(1)	0.2797(1)	0.2354(1)	39(1)
O(1)	0.2252(3)	0.3235(2)	0.2164(2)	45(2)
O(2)	0.4793(3)	0.3779(3)	0.3927(2)	52(2)
C(1)	0.0950(5)	0.2831(5)	0.0811(4)	62(2)
C(2)	0.6359(5)	0.3917(5)	0.4655(5)	76(3)
C(11)	0.3352(4)	0.1379(4)	0.5521(3)	41(2)
C(12)	0.3601(4)	0.0530(4)	0.6209(4)	49(2)
C(13)	0.4709(5)	0.1089(5)	0.7604(4)	74(3)
C(14)	0.5551(5)	0.2486(5)	0.8333(4)	60(3)
C(15)	0.5312(5)	0.3338(4)	0.7670(4)	62(3)
C(16)	0.4215(5)	0.2794(4)	0.6270(4)	52(2)
C(21)	0.0650(4)	−0.1455(3)	0.2923(3)	43(2)
C(22)	−0.0945(5)	−0.2203(4)	0.2569(4)	64(2)
C(23)	−0.1646(5)	−0.3622(4)	0.2130(4)	64(2)
C(24)	−0.0799(6)	−0.4303(4)	0.2033(4)	68(3)
C(25)	0.0762(6)	−0.3581(4)	0.2354(4)	67(3)
C(26)	0.1492(5)	−0.2170(4)	0.2801(4)	54(2)
C(31)	0.0136(4)	0.1209(4)	0.3130(4)	40(2)
C(32)	−0.1174(5)	0.0620(4)	0.1803(4)	53(2)
C(33)	−0.2284(5)	0.1089(5)	0.1459(5)	67(3)

Table 43 continued

	x	y	z	U_{eq} (Å² x 10³)
C(34)	-0.2089(6)	0.2173(5)	0.2444(6)	76(4)
C(35)	-0.0823(6)	0.2758(5)	0.3767(6)	73(3)
C(36)	0.0294(5)	0.2281(4)	0.4114(4)	56(3)

Table 44 Bond Distances and Angles of $(C_6H_5)_2Ge[S_2P(OCH_3)_2]$ (17)

Distances (Å)

Ge-S(1)	2.285(1)	Ge---S(2)	5.253(1)
Ge-C(11)	1.950(5)	ring C(11)-C(16)	
Ge-C(21)	1.944(5)	mean C-C	1.380(8)
Ge-C(31)	1.930(5)	ring C(21)-C(26)	
S(1)-P	2.060(2)	mean-C-C	1.383(9)
S(2)-P	1.923(2)	ring C(31)-C(36)	
P-O(1)	1.580(3)	mean C-C	1.381(9)
P-O(2)	1.578(3)		
O(1)-C(1)	1.433(6)		
O(2)-C(2)	1.421(6)		

Angles (°)

S(1)-Ge-C(11)	111.9(1)	ring C(11)-C(16)	
S(1)-Ge-C(21)	98.7(1)	mean C-C-C	120.0(5)
S(1)-Ge-C(31)	108.3(1)	ring C(21)-C(26)	
C(11)-Ge-C(21)	110.6(2)	mean C-C-C	120.0(6)
C(11)-Ge-C(31)	114.4(2)	ring C(31)-C(36)	
C(21)-Ge-C(31)	111.8(2)	mean C-C-C	120.0(6)

Table 44 continued

Ge-S(1)-P	109.0(1)	P-O(2)-C(2)	121.2(4)
S(1)-P-S(2)	109.1(1)	Ge-C(11)-C(12)	118.6(4)
S(1)-P-O(1)	109.2(1)	Ge-C(11)-C(16)	122.6(4)
S(2)-P-O(1)	116.3(1)	Ge-C(21)-C(22)	120.7(4)
S(1)-P-O(2)	108.6(1)	Ge-C(21)-C(26)	120.7(4)
S(2)-P-O(2)	117.2(2)	Ge-C(31)-C(32)	119.8(4)
O(1)-P-O(2)	95.7(2)	Ge-C(31)-C(36)	121.7(4)
P-O(1)-C(1)	120.2(3)		

Table 45 Final Fractional Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms of $(C_6H_5)_2Ge[S_2P(OCH_3)_2]_2$ (18)

	x	y	z	U_{eq} ($Å^2 \times 10^3$)
Ge	0.40012(8)	0.12913(7)	0.25677(6)	41.2(5)
S(1)	0.2902(2)	0.1033(2)	-0.1002(2)	61(1)
S(2)	0.1846(3)	0.2870(3)	-0.1109(2)	82(2)
S(3)	0.4675(2)	-0.0772(2)	0.3127(2)	59(1)
S(4)	0.3241(3)	-0.3346(2)	0.3979(2)	74(2)
P(1)	0.2740(2)	0.2836(2)	0.0256(2)	55(1)
P(2)	0.2896(2)	-0.1564(2)	0.3530(2)	59(1)
O(1)	0.1884(10)	0.3683(8)	-0.1271(7)	126(7)
O(2)	0.4049(7)	0.3474(7)	0.0243(6)	91(5)
O(3)	0.1843(7)	-0.0668(6)	0.4285(7)	96(5)
O(4)	0.2163(8)	-0.1339(7)	0.2358(6)	109(6)
C(1)	0.1585(12)	0.4963(10)	0.1321(10)	104(9)
C(2)	0.5146(9)	0.3134(12)	-0.0648(9)	104(9)

Table 45 continued

	x	y	z	U_{eq} (Å² x 10³)
C(3)	0.2076(13)	−0.0564(10)	0.5493(8)	108(7)
C(4)	0.0889(10)	−0.1569(10)	0.2206(9)	86(7)
C(11)	0.2822(8)	0.2253(7)	0.3740(6)	49(4)
C(12)	0.1406(8)	0.2459(8)	0.3723(7)	62(5)
C(13)	0.0625(10)	0.3120(10)	0.4618(10)	85(7)
C(14)	0.1260(14)	0.3552(10)	0.5523(9)	91(6)
C(15)	0.2669(13)	0.3347(10)	0.5520(8)	88(8)
C(16)	0.3448(10)	0.2693(8)	0.4634(7)	67(7)
C(21)	0.5757(7)	0.1901(7)	0.2180(6)	44(4)
C(22)	0.5931(9)	0.3181(8)	0.2411(7)	62(5)
C(23)	0.7232(12)	0.3603(11)	0.2103(9)	85(8)
C(24)	0.8270(11)	0.2757(13)	0.1560(9)	89(8)
C(25)	0.8092(9)	0.1507(11)	0.1312(8)	80(7)
C(26)	0.6835(8)	0.1089(8)	0.1631(7)	58(5)

Table 46 Bond Distances and Angles of $(C_6H_5)_2Ge[S_2P(OCH_3)_2]_2$ (18)

Distances (Å)

Ge-S(1)	2.257(2)	O(1)-C(1)	1.319(11)
Ge-S(3)	2.253(2)	O(2)-C(2)	1.455(10)
Ge-C(11)	1.931(7)	O(3)-C(3)	1.475(10)
Ge-C(21)	1.931(7)	O(4)-C(4)	1.330(10)
S(1)-P(1)	2.043(3)	ring C(11)-C(16)	
S(2)-P(1)	1.898(3)	mean C-C	1.381(12)
S(3)-P(2)	2.045(3)	ring C(21)-C(26)	
S(4)-P(2)	1.904(3)	mean C-C	1.387(12)
P(1)-O(1)	1.609(8)	Ge--S(3)	5.363(2)
P(1)-O(2)	1.520(6)	Ge--S(1)	5.398(2)
P(2)-O(3)	1.530(7)		
P(2)-O(4)	1.614(7)		

Angles (°)

S(1)-Ge-S(3)	103.4(1)	S(4)-P(2)-O(3)	117.1(3)
S(1)-Ge-C(11)	112.7(2)	S(3)-P(2)-O(4)	100.8(3)
S(3)-Ge-C(11)	111.3(2)	S(4)-P(2)-O(4)	113.9(3)
S(1)-Ge-C(21)	111.1(2)	O(3)-P(2)-O(4)	98.3(4)
S(3)-Ge-C(21)	101.3(2)	P(1)-O(1)-C(1)	127.4(8)
C(11)-Ge-C(21)	115.8(3)	P(1)-O(2)-C(2)	119.1(6)
Ge-S(1)-P(1)	103.7(1)	P(2)-O(3)-C(3)	118.4(7)
Ge-S(3)-P(2)	105.6(1)	P(2)-O(4)-C(4)	125.2(7)

Table 46 continued

S(1)–P(1)–S(2)	111.9(1)	Se–C(11)–C(12)	122.2(6)
S(1)–P(1)–O(1)	99.6(3)	Se–C(11)–C(16)	117.3(6)
S(2)–P(1)–O(1)	114.7(4)	Se–C(21)–C(22)	120.1(6)
S(1)–P(1)–O(2)	113.6(3)	Se–C(21)–C(26)	120.5(6)
S(2)–P(1)–O(2)	117.6(3)	ring C(11)–C(16)	
O(1)–P(1)–O(2)	97.1(5)	mean C–C–C	120.0(9)
S(3)–P(2)–S(4)	112.4(1)	ring C(21)–C(26)	
S(3)–P(2)–O(3)	112.4(3)	mean C–C–C	120.0(8)

Table 47 Final Fractional Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms of $C_4H_5Ge[S_2P(OCH_3)_2]_3$ (19)

	x	y	z	U_{eq} ($Å^2 \times 10^3$)
Ge	0.1138(2)	0.2500(0)	0.2162(2)	55(2)
S(1)	0.2158(3)	0.1344(3)	0.2569(4)	72(3)
S(2)	0.2104(5)	−0.0889(3)	0.2345(5)	92(4)
S(3)	−0.0255(5)	0.2500(0)	0.3070(6)	84(5)
S(4A)	0.1402(16)	0.2500(0)	0.4870(17)	111(7)
S(4B)	−0.0768(15)	0.2500(0)	0.5506(16)	107(6)
P(1)	0.1551(4)	0.0221(4)	0.1838(4)	64(2)
P(2)	0.0144(9)	0.2182(8)	0.4524(9)	86(4)
O(1)	0.0414(10)	0.0358(11)	0.1905(13)	108(12)
O(2)	0.1723(15)	0.0412(11)	0.0670(12)	118(13)
O(3)	0.0222(32)	0.1101(28)	0.4590(29)	392(19)
C(1A)	−0.0140(35)	−0.0166(33)	0.2688(39)	118(15)
C(1B)	−0.0401(48)	−0.0068(45)	0.1744(51)	100(20)
C(2A)	0.2721(47)	0.0086(45)	0.0175(44)	158(21)
C(2B)	0.1536(55)	−0.0001(58)	−0.0147(62)	110(27)
C(3)	−0.1081(78)	0.0774(76)	0.4698(72)	301(44)
C(11)	0.0791(28)	0.2500(0)	0.0745(26)	79(23)
C(12)	0.1462(24)	0.2500(0)	0.0016(25)	78(23)
C(13)	0.1293(43)	0.2500(0)	−0.0909(48)	150(48)
C(14)	0.0373(48)	0.2500(0)	−0.1182(29)	106(33)
C(15)	−0.0459(39)	0.2500(0)	−0.0588(38)	163(45)
C(16)	−0.0228(27)	0.2500(0)	0.0437(26)	91(24)

Table 48 Anisotropic Thermal Parameters[a,b] ($Å^2 \times 10^3$) for $C_4H_5Ge[S_2P(OCH_3)_2]_3$ (19)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ge	48(1)	54(2)	59(2)	0(0)	-5(1)	0(0)
S(1)	64(3)	59(3)	88(4)	7(2)	-23(3)	-7(3)
S(2)	117(4)	57(3)	97(4)	9(3)	-21(4)	9(3)
S(3)	50(4)	103(6)	95(6)	0(0)	2(4)	0(0)
P(1)	68(3)	53(3)	70(3)	4(3)	-7(3)	-3(3)
O(1)	67(9)	98(12)	157(16)	-3(9)	-24(10)	6(11)
O(2)	222(21)	73(10)	69(10)	25(12)	-18(12)	7(9)
C(11)	126(29)	44(16)	92(25)	0(0)	-50(23)	0(0)
C(12)	71(21)	133(32)	44(17)	0(0)	1(17)	0(0)
C(13)	163(50)	102(33)	173(62)	0(0)	47(45)	0(0)
C(14)	223(58)	55(20)	57(21)	0(0)	-12(34)	0(0)
C(15)	145(44)	201(53)	133(40)	0(0)	-107(36)	0(0)
C(16)	107(27)	82(24)	99(26)	0(0)	-41(22)	0(0)

a Anisotropic temperature factors are of the form:

$\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$

b Atoms S(4A), S(4B), P(2), O(3), C(1A), C(1B), C(2A), C(2B) and C(3) were refined isotropically.

Table 49 Bond Distances and Angles of $C_4H_8Ge[S_2P(OCH_3)_2]_2$ (19)

Distances (Å)

Ge–S(1)	2.251(5)	P(1)–O(2)	1.58(2)
Ge–S(3)	2.248(8)	P(2)–O(3)	1.58(4)
Ge–C(11)	1.92(3)	O(1)–C(1A)	1.49(5)
S(1)–P(1)	2.071(7)	O(1)–C(1B)	1.29(6)
S(2)–P(1)	1.906(7)	O(2)–C(2A)	1.58(6)
S(3)–P(2)	2.04(1)	O(2)–C(2B)	1.26(8)
S(4A)–P(2)	1.84(2)	O(3)–C(3)	1.85(9)
S(4B)–P(2)	1.86(2)	ring C(11)–C(16)	
P(1)–O(1)	1.57(1)	mean C–C	1.35(7)

Angles (°)

S(1)–Ge–S(3)	113.5(2)	S(4A)–P(2)–S(4B)	113(1)
S(1)–Ge–C(11)	112.5(7)	S(3)–P(2)–O(3)	107(2)
S(3)–Ge–C(11)	108(1)	S(4A)–P(2)–O(3)	100(2)
S(1)–Ge–S(1)	96.8(3)	S(4B)–P(2)–O(3)	105(2)
Ge–S(1)–P(1)	103.4(2)	P(1)–O(1)–C(1A)	119(2)
Ge–S(3)–P(2)	105.8(5)	P(1)–O(1)–C(1B)	142(3)
S(1)–P(1)–S(2)	110.4(3)	P(1)–O(2)–C(2A)	118(2)
S(1)–P(1)–O(1)	105.7(7)	P(1)–O(2)–C(2B)	136(4)
S(2)–P(1)–O(1)	118.8(7)	P(2)–O(3)–C(3)	101(4)
S(1)–P(1)–O(2)	104.7(7)	Ge–C(11)–C(12)	122(3)
S(2)–P(1)–O(2)	115.5(7)	Ge–C(11)–C(16)	118(3)
O(1)–P(1)–O(2)	100(1)	ring C(11)–C(16)	
S(3)–P(2)–S(4A)	115.1(9)	mean C–C–C	120(6)
S(3)–P(2)–S(4B)	114.6(9)		

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